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PREDICTING EQUILIBRIA FOR SINGLE SOLUTE AND MULTICOMPONENT AQUEOUS-PHASE ADSORPTION ONTO ACTIVATED CARBON

by

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16. ABSTRACT

Granular activated carbon (GAC) is useful for removing potentially harmful synthetic organic chemical (SOCs) found in drinking water sources. In the design of fixed-bed contacters, equilibrium considerations govern the usage rate of the carbon, while mass transfer considerations control the size and configuration of the contacter. This research deals with equilibrium considerations for single and multicomponent adsorption.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

In the design of fixed-bed contacters, equilibrium considerations govern the usage rate of granular activated carbon, while mass transfer considerations control the size and configuration of the contacter. The research reported here deals with equilibrium considerations for single and multicomponent adsorption.

Frances T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

Granular activated carbon (GAC) is useful for removing potentially harmful synthetic organic chemicals (SOCs) found in drinking water sources. In the design of fixed-bed contacters, equilibrium considerations govern the usage rate of the carbon, while mass transfer considerations control the size and configuration of the contacter. This thesis deals with equilibrium considerations for single and multicomponent adsorption.

The capability of the Polanyi adsorption potential theory and Urano's modified Freundlich equation to correlate single solute isotherms of hydrophobic compounds is tested. Of the two methods, only the correlation curves which were proposed by Polanyi coincide and form a general correlation. The correlation relates volume of chemical adsorbed per unit mass of carbon to the chemical's adsorption potential divided by its molar volume. Accordingly, the correlation is used to calculate the Freundlich isotherm parameters for other hydrophobic compounds knowing only the density and solubility of the solute. Two granular activated carbons, and ten hydrophobic compounds including both aliphatics and aromatics are used to test the correlation.

Three models are used to predict the effect of temperature on isotherms. They are Urano's modified Freundlich equation, the Polanyi adsorption potential theory, and the Clausius-Clapeyron equation. All three methods give essentially the same prediction for the effect of temperature.

Ideal adsorbed solution theory is used to predict the competitive interactions between VOCs in the Wausau, WI groundwater. The Wausau, WI groundwater contains a high concentration of total organic carbon

(TOC). However, this is ignored and only the known VOCs are used to calculate the competitive effects.

Because of the large number of unknown compounds which are present in the Wausau groundwater, the use of hypothetical components to represent the adsorption strength of these unknown compounds is studied. The hypothetical components are obtained by fitting either a raw water isotherm for a single component or by fitting a TOC isotherm. The hypothetical component parameters are then used to predict the background competition for identified compounds in the water.

The equilibrium column model (ECM) is a fixed bed adsorption model that ignores mass transfer resistances. The proposed ECM uses ideal adsorbed solution theory to predict the competitive effects in multicomponent mixtures. Pilot plant data found in Wausau, WI is compared to the ECM predictions. With the ECM, one can determine the elution order of the adsorbates, the lowest carbon usage rate in multicomponent mixtures, and the highest overshoot concentrations. Also, one can use the ECM to reduce the number of chemical components to be specified in mass transfer models.

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I. INTRODUCTION

Granular activated carbon (GAC) is useful for removing potentially harmful synthetic organic chemicals (SOCs) found in drinking water sources. Adsorption equilibrium governs the carbon usage rate in a fixed-bed contacter, whereas, mass transfer effects govern the configuration or size of the contacter. This thesis deals with defining the equilibrium effects for multicomponent adsorption.

Multicomponent adsorption can be modeled using ideal adsorbed solution theory (IAST) (Radke and Prausnitz, 1972). IAST requires that the water-phase concentrations and Freundlich single solute isotherm parameters be known for the entire matrix of adsorbing compounds present in the water.

To avoid the tedium of running single solute isotherms for every compound present in the groundwater, The Polanyi adsorption potential theory is used to correlate single solute isotherm data of hydrophobic compounds. From this correlation, good estimates of Freundlich isotherm parameters can be calculated when the molecular weight, density, and solubility of the compound of interest is known. The classes of compounds that are used in the correlation include both aromatics and halogenated aliphatics.

The effect of temperature on isotherms is also predicted in hope of avoiding excessive single solute isotherm experiments. The methods used are the Polanyi adsorption potential theory, Urano's modified Freundlich equation, and the Clausius-Clapeyron equation.

Since it is an almost impossible task to determine the concentrations of all the adsorbing species present in a contaminated drinking water, the use of hypothetical components is evaluated.

Hypothetical components account for the adsorbing strength of the unknown compounds in the water by assuming that the unknown compounds behave collectively as one compound. The hypothetical components single solute Freundlich parameters can be determined by either fitting a raw water isotherm for a single component, or by fitting a TOC isotherm. Once the adsorption parameters for the hypothetical components are estimated, they are tested to see if they will predict the background competition for raw water isotherms completed for different components.

In a fixed bed column, adsorption will not behave as in a bottle point isotherm. Instead, the components will chromatographically separate through the column. To model this, the equilibrium column model (ECM) is used. The ECM is a fixed bed adsorption model that ignores mass transfer resistances. Multicomponent equilibrium is predicted by IAST. The ECM can be used to determine the elution order of the adsorbates, the lowest carbon usage rate in multicomponent mixtures, and the highest overshoot concentrations. Also, the ECM can be used to reduce the number of components to be specified in mass transfer models. The ECM is not restricted to known components, but can make predictions using hypothetical components as well.

II. SINGLE SOLUTE EQUILIBRIUM STUDIES

Temperature, equilibration time, and pH can have large influences on the results of an isotherm. This section discusses the effect of these conditions using isotherms which were completed at Michigan Technological University. This information will allow the determination of which isotherms should be used for modeling of multicomponent adsorption.

The isotherms completed at Michigan Technological University (Ari, 1982) (Luft, 1983) (Berrigan, 1985) (Kato, 1985) are shown in Tables II-1 and II-2 for Westvaco (WV-G) and Calgon Filtrasorb 400 carbon (F-400); respectively. All the single solute isotherms were conducted according to the procedure presented in Appendix III. The isotherm data tables are presented in Appendix IV. Since our modeling emphasis is on F-400 carbon, more isotherms were completed on F-400 carbon than on WV-G carbon.

A. REQUIRED TIME TO ACHIEVE EQUILIBRIUM

Figure II-1 compares trichloroethene (TCE) isotherms which have equilibration times of 3.0 days and 6.5 days on WV-G carbon. As shown, the isotherm which was equilibrated for 3.0 days suggests that equilibrium had not been achieved because the isotherm has a lower capacity than the isotherm which was equilibrated for 6.5 days, and because curvature is present in the isotherm which was equilibrated for 3.0 days. Figures II-2 through II-4 contain isotherms completed on 5-1-82 and 6-1-82 for TCE, chloroform, and bromoform on F-400 carbon. The difference between the 5-1-82 and 6-1-82 isotherms is that the 5-1-82 isotherms had an equilibration time of 2 days, while the 6-1-82

Table II-1. Summary of the Single Component Isotherms, Experimental Conditions, and Freundlich Isotherm Parameters.

Carbon Type, Mesh Size, Temperature, Water Matrix	Compound	Equilibration Time, pH	K(um/g)$(L/um)^{1/n}$ Best Fit	95% Confidence Interval K	1/n Best Fit	95% Confidence Interval 1/n	Concentration Range (um/L)
WV-G	Cis-1,2 Dichloroethene	7.0 days pH = 6.0*	35.4	23.1 - 56.6	0.6441	0.6045 - 0.6383	1.48 - 13.8
200 x 400	Trichloroethene	6.5 days pH = 6.0*	181.0	148.4 - 220.3	0.4073	0.3850 - 0.4295	0.04 - 0.91
$10^oC \pm 1^oC$	Trichloroethene	3.0 days pH = 6.0*	148.4	107.3 - 205.1	0.3944	0.3561 - 0.4327	0.03 - 3.05
Milli-Q Water	Tetrachloroethene	6.0 days pH = 6.0*	589.5	460.8 - 753.7	0.5017	0.4762 - 0.5271	0.04 - 5.49
Luft (1983)							

*Buffered with 10^{-3} M Phosphate Buffer

Table II-2. Summary of the Single Component Isotherms, Experimental Conditions and Freundlich Isotherm Parameters.

Carbon Type, Mesh Size, Temperature, Water Matrix	Compound	Equilibration Time, pH	K(um/g) $(L/um)^{1/n}$ Best Fit	95% Confidence Interval K	1/n Best Fit	95% Confidence Interval 1/n	Concentration Range (um/L)
F-400	Cis-1,2 Dichloroethene	7.0 days pH = 6.0*	39.0	26.7 - 57.1	0.7045	0.6687 - 0.7402	1.2 - 12.9
200 x 400	Trichloroethene	6.5 days pH = 6.0*	196.6	124.4 - 310.6	0.4163	0.3620 - 0.4706	0.043 - 2.74
$10^{0}C \pm 1^{0}C$	Tetrachloroethene	6.0 days pH = 6.0*	650.6	530.1 - 798.9	0.4579	0.4365 - 0.4794	0.021 - 7.05
Milli-Q Water	Bromoform	10 days pH = 6.0*	160.5	142.9 - 180.3	0.5629	0.5528 - 0.5730	0.152 - 7.79
Luft (1983)	Chloroform	7 days pH = 6.0*	30.4	24.5 - 37.9	0.5325	0.5102 - 0.5549	0.021 - 9.88
	1-2, Dibromoethane	7 days pH = 6.0*	118.4	98.5 - 142.4	0.4808	0.4637 - 0.4979	0.170 - 11.0
	Chlorodibromomethane	7 days pH = 6.0*	96.0	59.8 - 154.2	0.5170	0.4758 - 0.5581	0.441 - 8.78
F-400	Cis-1,2 Dichloroethene	28 days pH = 7.5-8	46.9	46.2 - 47.6	0.5562	0.5509 - 0.5616	0.117 - 55.5
200 x 400	Trichloroethene	31 days pH = 7.5-8	191.7	186.5 - 196.9	0.4328	0.4195 - 0.4462	0.114 - 23.6
$13.8^{0}C \pm 1^{0}C$	Tetrachloroethene	33 days pH = 7.5-8	435.2	425.9 - 444.4	0.3847	0.3721 - 0.3973	0.161 - 47.2
Milli-Q Water	Ethyl benzene	21 days pH = 7.5-8	714.4	682.3 - 746.3	0.2953	0.2759 - 0.3147	0.04 - 26.6
Kato (1985)	m-xylene	21 days pH = 7.5-8	1044.0	977.2 -1110.0	0.2458	0.2237 - 0.2679	0.36 - 35.7
	o-xylene	26 days pH = 7.5-8	894.6	851.0 - 938.3	0.2587	0.2369 - 0.2806	0.5 - 41.3
	Toluene	25 days pH = 7.5-8	475.1	467.5 - 482.8	0.3282	0.3213 - 0.3351	0.06 - 37.5
F-400							
60 x 80							
$13.0^{0}C \pm 1^{0}C$	Trichloroethene	14 days pH = 7.5	187.5	142.8 - 246.1	0.4179	0.2875 - 0.5483	1.93 - 21.3
Milli-Q Water							
Berrigan (1985)							

(Continued)

Table II-2. (Continued) Summary of the Single Component Isotherms, Experimental Conditions and Freundlich Isotherm Parameters.

Carbon Type, Mesh Size, Temperature, Water Matrix	Compound	Equilibration Time, pH	$K(\mathrm{um/g})(\mathrm{L/um})^{1/n}$ Best Fit	95% Confidence Interval K	1/n Best Fit	95% Confidence Interval 1/n	Concentration Range (um/L)
F-400 <200 Mesh 20 - 22^{0}C Milli-Q Water Ari (1982)	Chloroform	2 days pH = 6.0*	12.19	11.87 - 12.50	0.7556	0.7387 - 0.7725	0.289 - 11.1
	Trichloroethene	2 days pH = 6.0*	93.66	85.00 - 103.2	0.4696	0.4216 - 0.5177	0.024 - 4.02
	Bromoform	2 days pH = 6.0*	78.17	78.17 - 81.64	0.6889	0.6640 - 0.7139	0.047 - 15.3
F-400 40 x 60 mesh 20 - 22^{0}C Milli-Q Water Ari (1982)	Chloroform	6.4 days pH = 6.0*	14.15	8.00 - 20.69	0.6589	0.5628 - 0.8127	0.327 - 49.2
	Trichloroethene	6.4 days pH = 6.0*	114.1	96.25 - 131.1	0.5157	0.4663 - 0.5873	0.004 - 26.9
	Bromoform	6.4 days pH = 6.0*	92.39	86.25 - 97.92	0.5987	0.5596 - 0.6471	0.017 - 14.6

* Buffered with 1×10^{-3} M phosphate buffer.

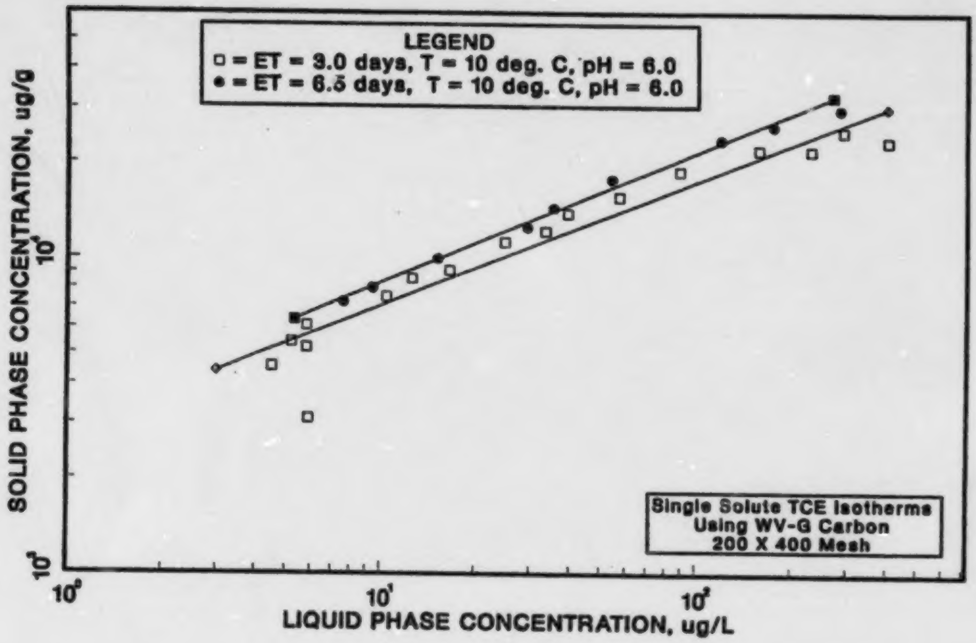

Figure II-1. Single Solute Isotherm Data for Trichloroethene on WV-G Carbon.

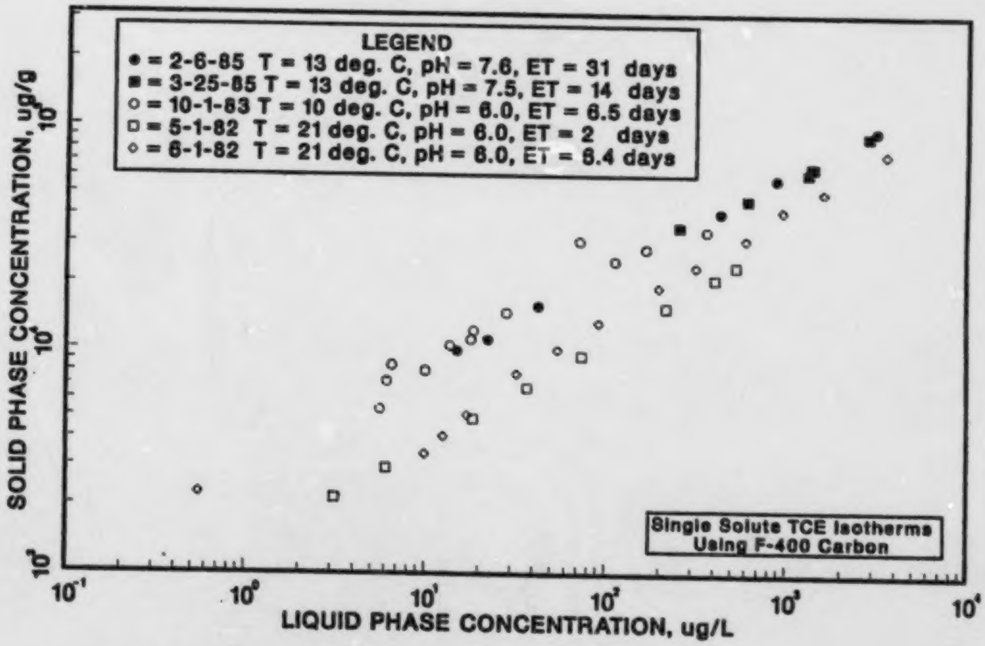

Figure II-2. Single Solute Isotherm Data for Trichloroethene on F-400 Carbon.

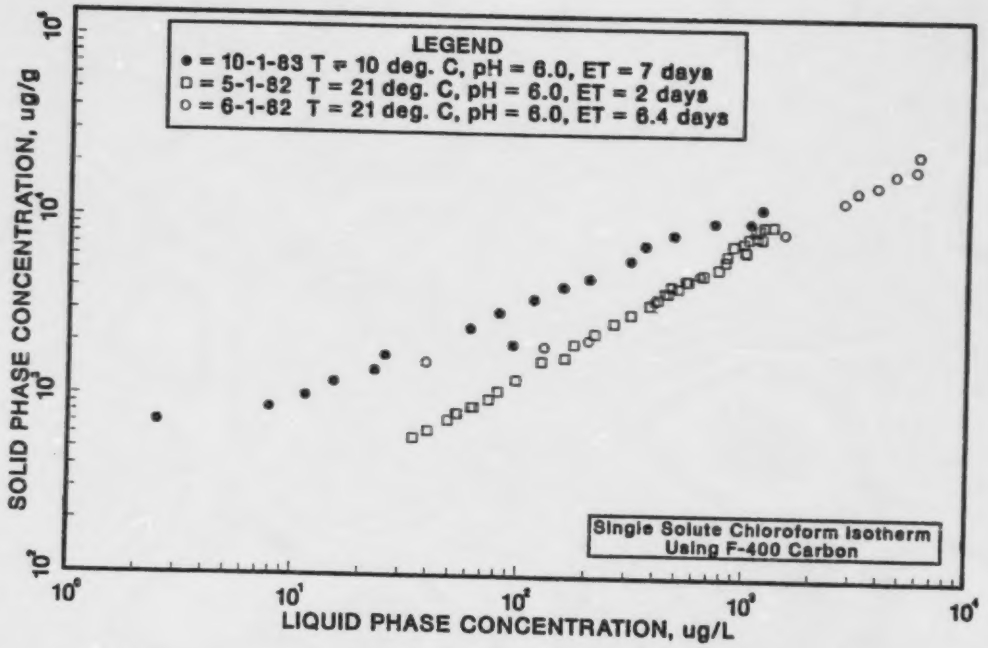

Figure II-3. Single Solute Isotherm Data for Chloroform on F-400 Carbon.

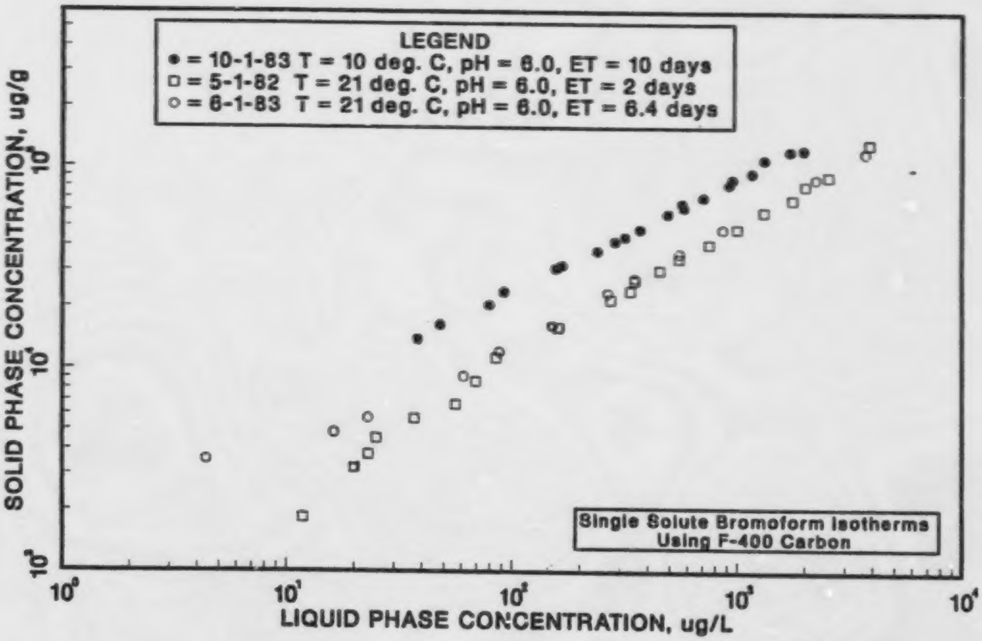

Figure II-4. Single Solute Isotherm Data for Bromoform on F-400 Carbon.

isotherms had an equilibration time of 6.4 days. The difference in equilibration times was shown to have no effect on the isotherms because the capacities are identical in each case. It is interesting to note that in Figures II-2 through II-4 the change of equilibration time from 2 days to 6.4 days does not show a change in capacities while in Figure II-1 the change in equilibration time from 3.0 days to 6.5 days does show a change in capacities. The reason for this can be either due to the fact that they were done on different carbons, or that because the temperature was higher for the F-400 isotherms (22°C) as compared to the WV-G isotherms (10°C), the F-400 isotherms came to equilibrium faster.

Figure II-2 also shows two 13.8°C F-400 carbon isotherms run for equilibration times of 14 and 31 days. The difference in capacities can be seen to be negligible. Therefore, for modeling purposes, the isotherms used to find the Freundlich isotherm parameters will have equilibration times greater than 6 days.

B. EFFECT OF TEMPERATURE

Shown in Figures II-2 through II-4 are 10°C isotherms compared to 21°C isotherms. As can be seen in all three figures, the 21°C isotherms show a notable decrease in capacity as expected. The isotherms also show an increase in slope with temperature, also as expected. However, it must be noted that the 10°C and 21°C isotherms were performed on different lots of carbon which may introduce a difference in capacities.

Plotted on Figures II-2, II-5, and II-6 are isotherms completed at 10°C and 13.8°C. Figures II-2 and II-5 for TCE and cis 1,2-dichloroethene (DCE), respectively, show no difference between the isotherms performed at 10°C and 13.8°C. Since the 10°C isotherms were

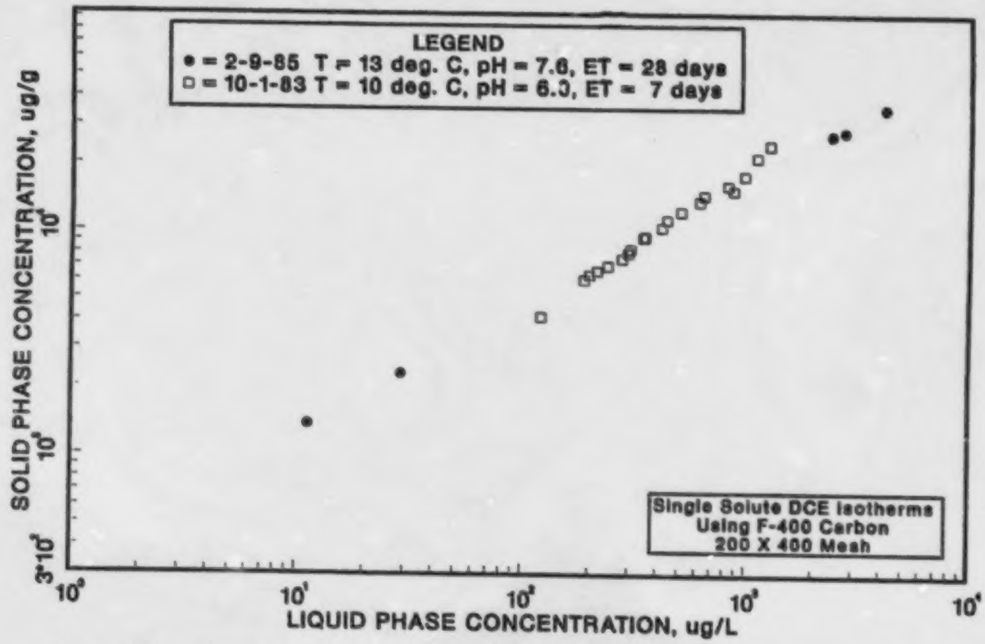

Figure II-5. Single Solute Isotherm Data for cis 1,2-Dichloroethene on F-400 Carbon.

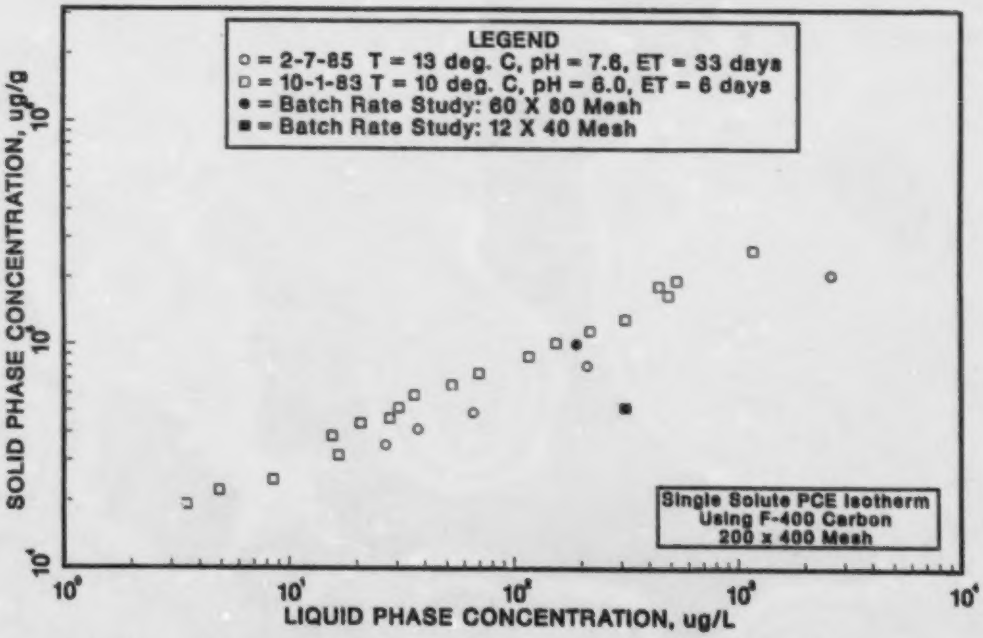

Figure II-6. Single Solute Isotherm Data for Tetrachloroethene on F-400 Carbon.

run at a pH of 6.0 and the 13.8°C isotherms were run at a pH of 7.6, it was assumed that the pH difference had little effect on the isotherms. This will be shown to be true in the following section. The tetrachloroethene (PCE) isotherms in Figure II-6 at 10°C and 13.8°C do show a distinct difference in capacities. If the difference is due to temperature, the slope of the 13.8°C isotherm should be slightly higher than the 10°C isotherm. This, however, is not the case. To help decide the matter, two PCE batch rate studies completed at 11°C (Dobrzelewski 1985) were plotted. The difference between the two was that one was completed using 12x40 mesh carbon, and the other was completed using 60x80 mesh carbon. The 12x40 mesh study was not run to equilibrium and hence its capacity fell below the line of the 2-7-85 isotherm. The 60x80 study fell in between the two isotherms indicating the difference could be due to temperature. However, this seems unlikely because DCE and TCE did not show a difference in capacities between 10°C and 13.8°C.

C. EFFECT OF pH

The capacity of isotherms has been shown to decrease a great deal as pH increases (Rosene and Manes, 1977). This was not observed for the isotherms run at Michigan Technological University, as shown in Figures II-2 and II-5. As discussed earlier, the equilibration time does not affect the isotherm after 6.0 days, and the temperature difference between 10°C and 13.8°C does not affect the isotherm. Therefore, the only reason for a difference between the 10°C isotherms and the 13.8°C isotherms is the effect of pH. Since there is no difference in these isotherms it can be concluded that pH difference did not affect the isotherms. One thing that should be mentioned is that there is no canceling effect between the temperature difference and the pH difference because an increase in temperature and an increase in pH would both decrease the capacity. The 13.8°C (higher temperature) isotherms were performed at the higher pH of 7.6, therefore, no canceling effect is possible.

D. ISOTHERMS USED FOR MULTICOMPONENT PREDICTIONS

The isotherms suitable for use in multicomponent predictions will have an equilibration time greater than 6 days, and will be completed between 10°C and 16°C which is the temperature range in the pilot plant located in Wausau, WI. Therefore, for DCE, the isotherm run on 2-9-85 will be used for modeling. This is shown on Figure II-7 with its Freundlich fit. For TCE, the isotherm run on 2-6-85 will be used as presented in Figure II-8 with its Freundlich fit.

To determine which PCE isotherm should be used for modeling, it is noticed that if the 10-1-83 isotherm is used in the equilibrium column model, as discussed in Section V, toluene would break through the column ahead of PCE. This would be reversed if the 2-7-85 isotherm were used. Therefore, since the pilot plant study shows that PCE breaks out of the column before toluene, the 2-7-85 isotherm should be used for modeling purposes. The plot of this isotherm can be seen in Figure II-9 with its Freundlich isotherm fit. For a final check, the Polanyi correlation as discussed in section III-B-2 confirmed that the 2-7-85 isotherm should be used for modeling because it correlated better than the 10-1-83 isotherm.

The following compounds have had only one single solute isotherm completed on F-400 carbon between 10°C and 16°C at Michigan Technological University: chloroform, bromoform, toluene, ethyl benzene, o-xylene, m-xylene, 1,2-dibromoethane, and

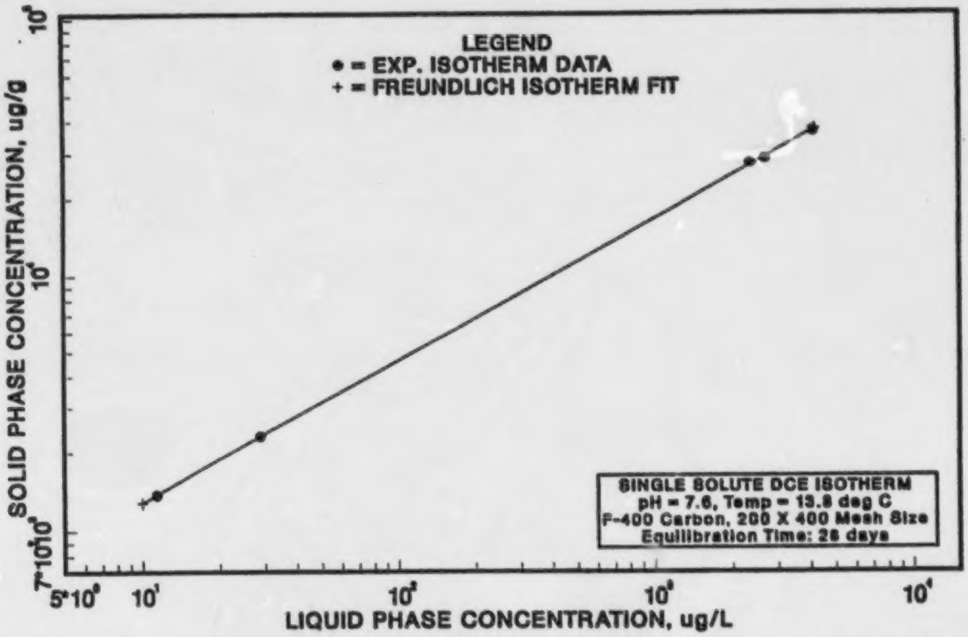

Figure II-7. Single Solute Isotherm Data and Freundlich Isotherm Fit for cis 1,2-Dichloroethene on F-400 Carbon.

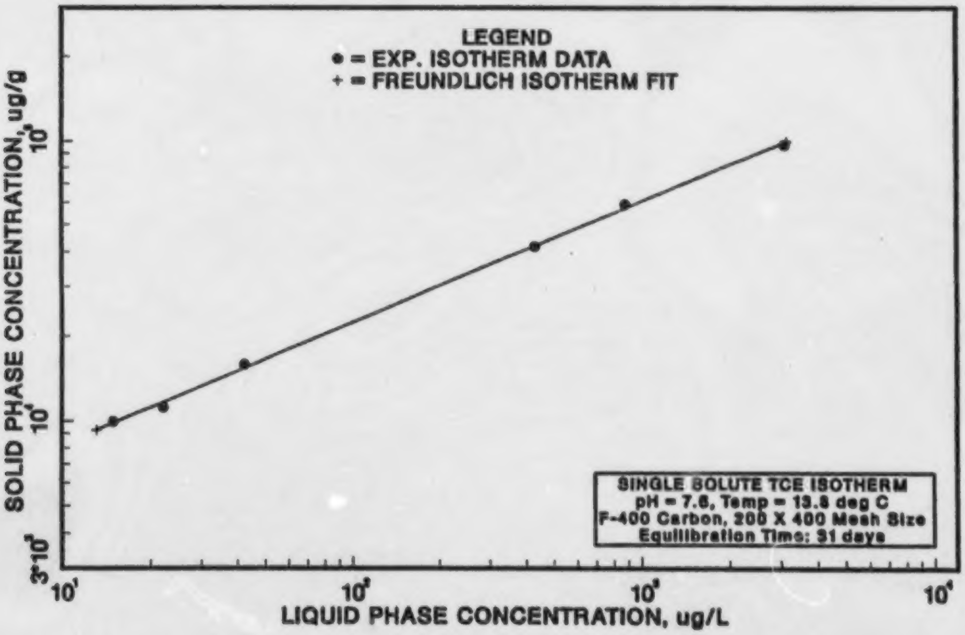

Figure II-8. Single Solute Isotherm Data and Freundlich Isotherm Fit for Trichloroethene on F-400 Carbon.

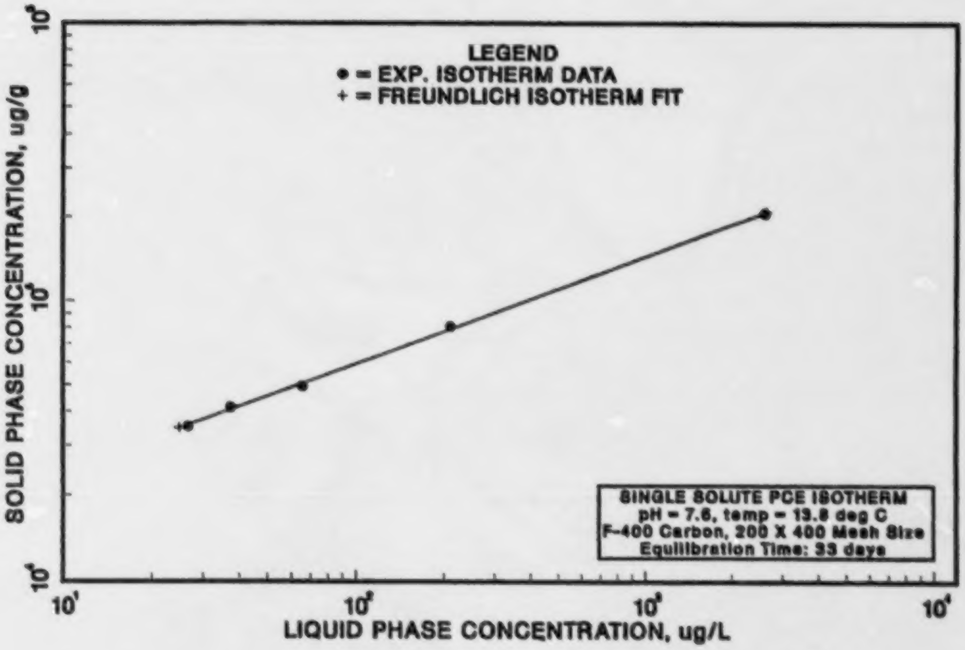

Figure II-9. Single Solute Isotherm Data and Freundlich Isotherm Fit for Tetrachloroethene on F-400 Carbon.

chlorodibromomethane. Since only one isotherm is available, the Freundlich parameters will be found from that isotherm. The plots of these isotherms are shown with their Freundlich fit in Figures II-10 through II-17, respectively. For WV-G carbon, the single solute isotherms used for DCE, TCE, and PCE are shown in Figures II-18 through II-20, respectively.

Upon looking at Table II-3, it can be noticed that DCE, bromoform, and chloroform do not follow the pattern of decreasing 1/n with increasing K as shown by Abe et al. (1982). However, this does not necessarily mean that these isotherms are in error because it is a general correlation, and K and 1/n change for different concentration ranges . A plot of 1/n versus K is shown in Figure II-21.

A comparison of the performance of the F-400 and WV-G carbons show that both have about the same adsorption strength. Examination of the equilibrium capacities, or Freundlich K, presented in Tables II-1 and II-2 show that for both carbons PCE has about 16 times the capacity of DCE and about 3 times the capacity of TCE. The Freundlich K's and 1/n's for these compounds appear to be within the experimental error of the isotherms. Therefore, since the carbon adsorbs these compounds in a like manner, the carbons can be assumed to be similar in adsorbing strength.

Table II-4 presents results of previously reported Freundlich isotherm parameters for TCE and PCE. If these values are compared to the parameters presented in Tables II-1 and II-2, it is found that the capacities determined in this study are much higher then those previously reported. There are several reasons that can explain the differences in the parameters:

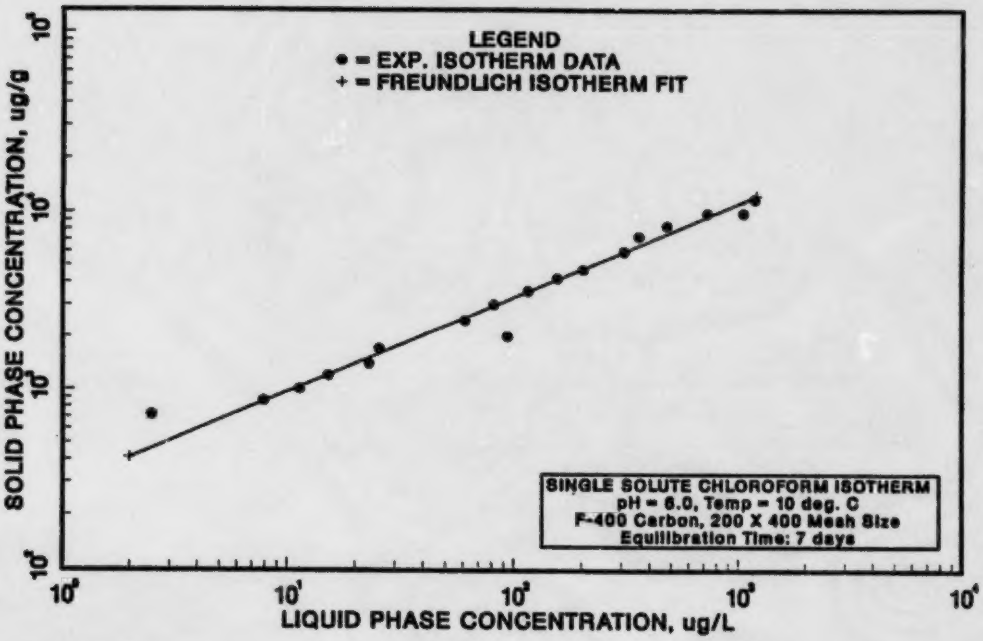

Figure II-10. Single Solute Isotherm Data and Freundlich Isotherm Fit for Chloroform on F-400 Carbon.

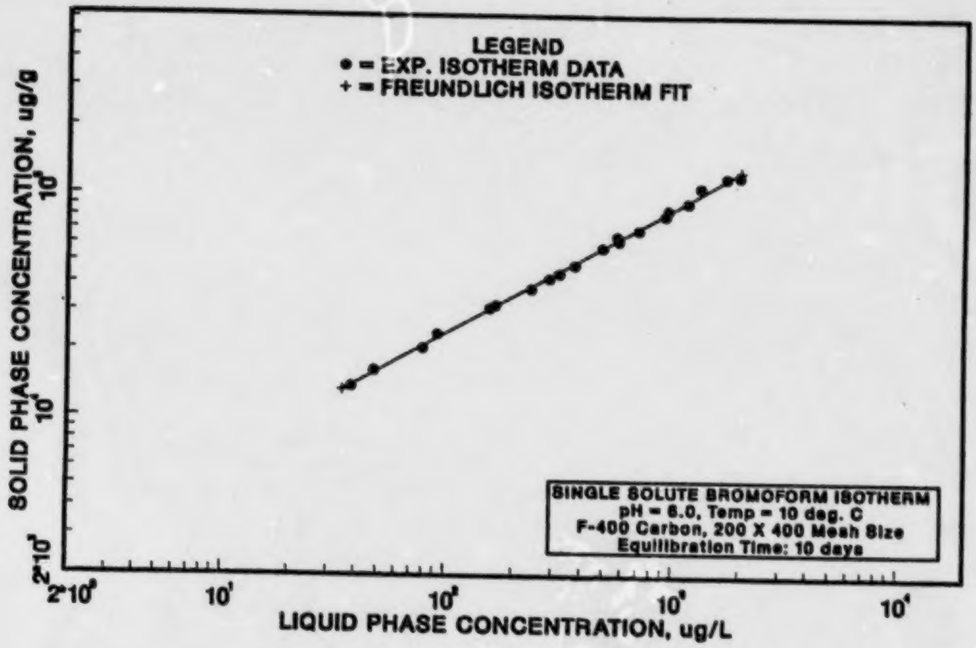

Figure II-11. Single Solute Isotherm Data and Freundlich Isotherm Fit for Bromoform on F-400 Carbon.

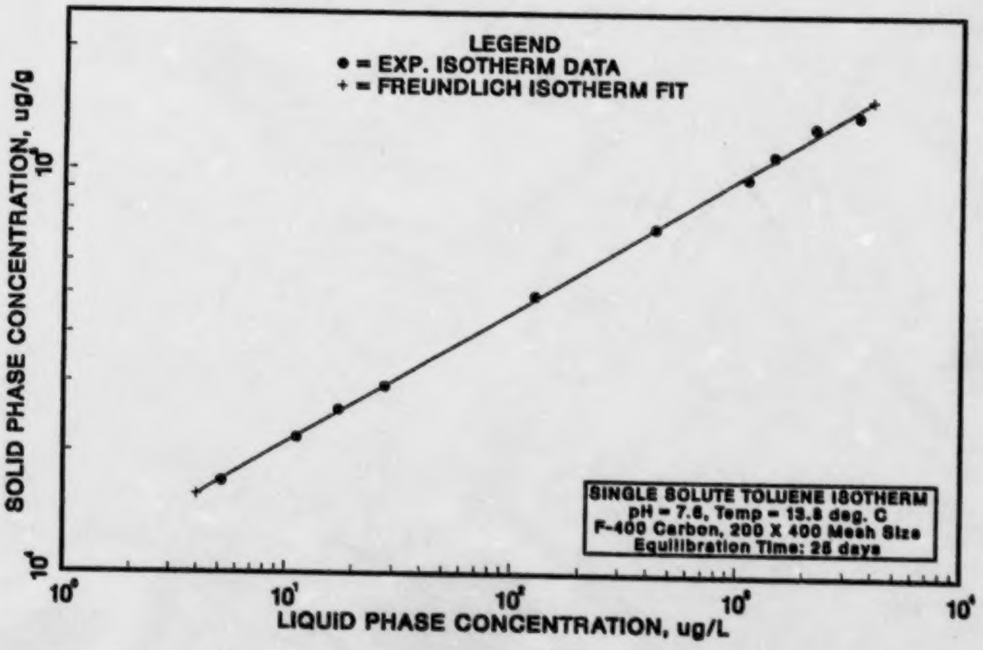

Figure II-12. Single Solute Isotherm Data and Freundlich Isotherm Fit for Toluene on F-400 Carbon.

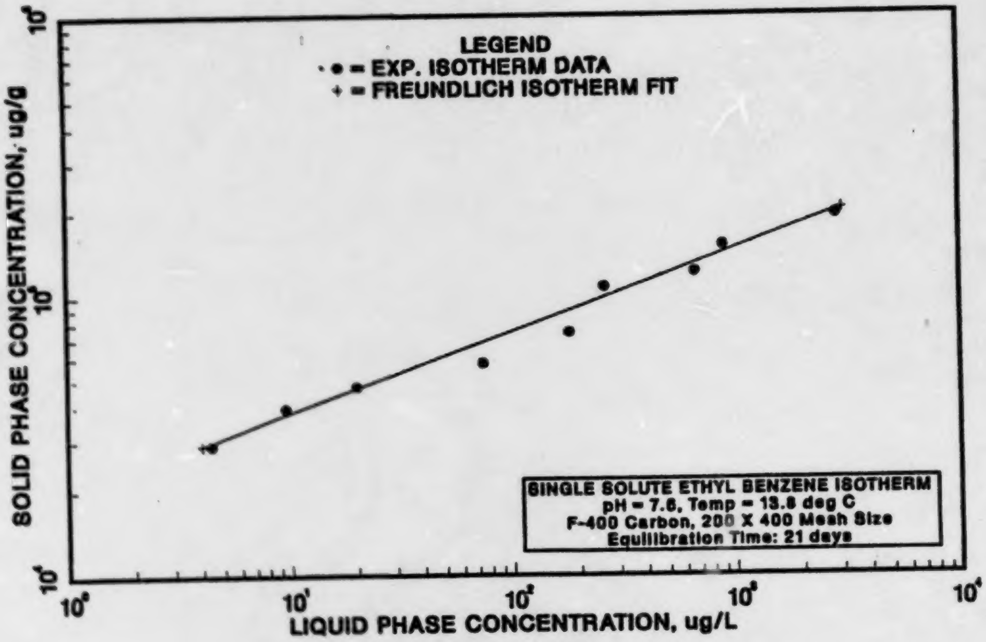

Figure II-13. Single Solute Isotherm Data and Freundlich Isotherm Fit for Ethyl Benzene on F-400 Carbon.

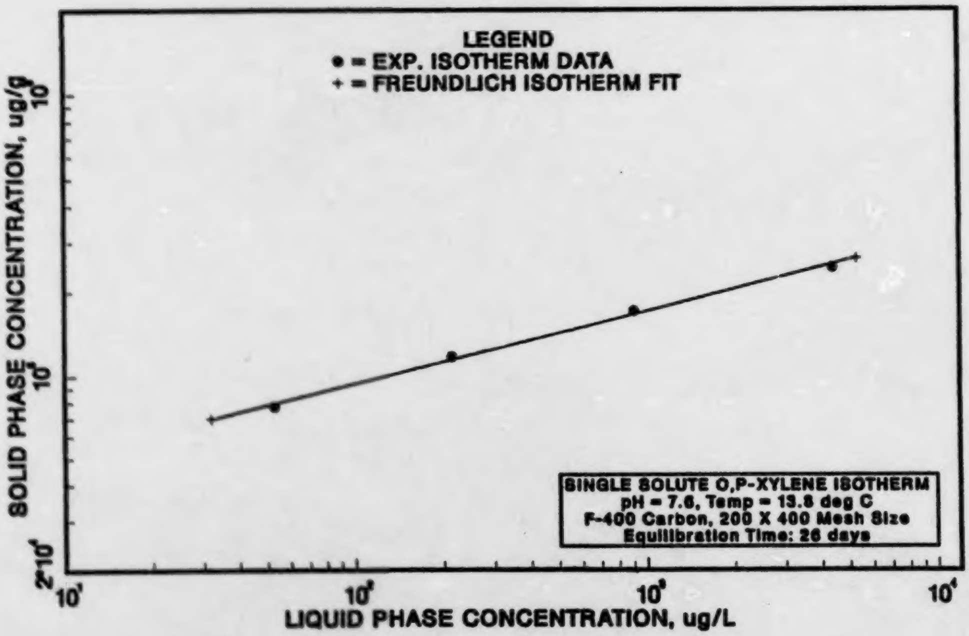

Figure II-14. Single Solute Isotherm Data and Freundlich Isotherm Fit for o,p-Xylene on F-400 Carbon.

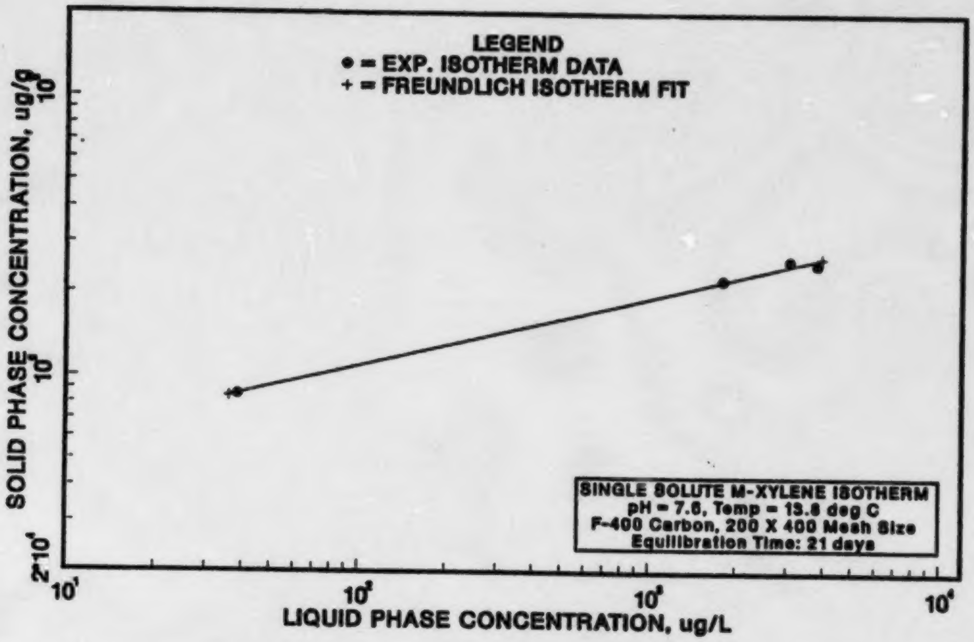

Figure II-15. Single Solute Isotherm Data and Freundlich Isotherm Fit for m-Xylene on F-400 Carbon.

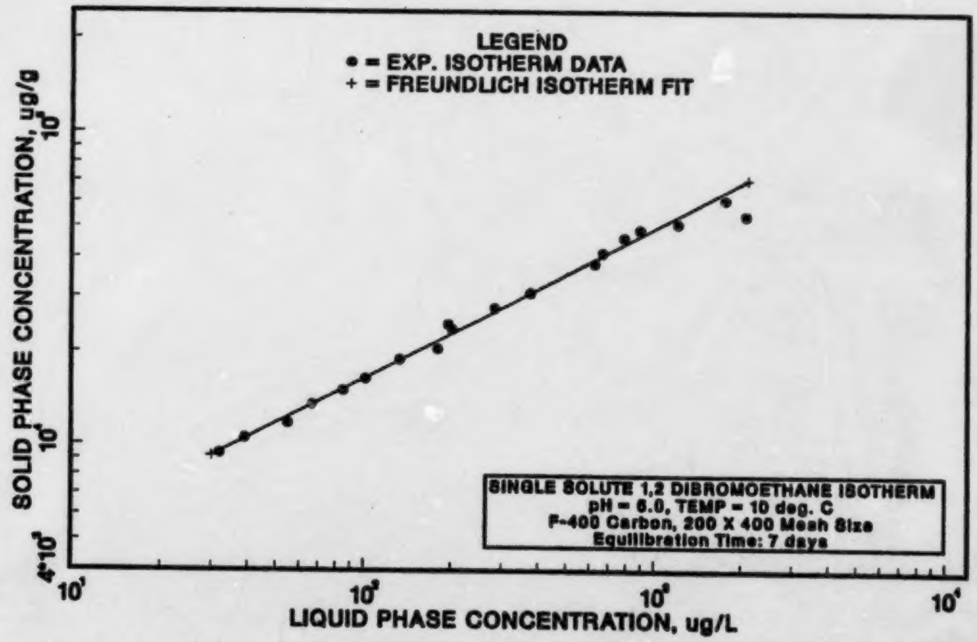

Figure II-16. Single Solute Isotherm Data and Freundlich Fit for 1,2-Dibromoethane on F-400 Carbon.

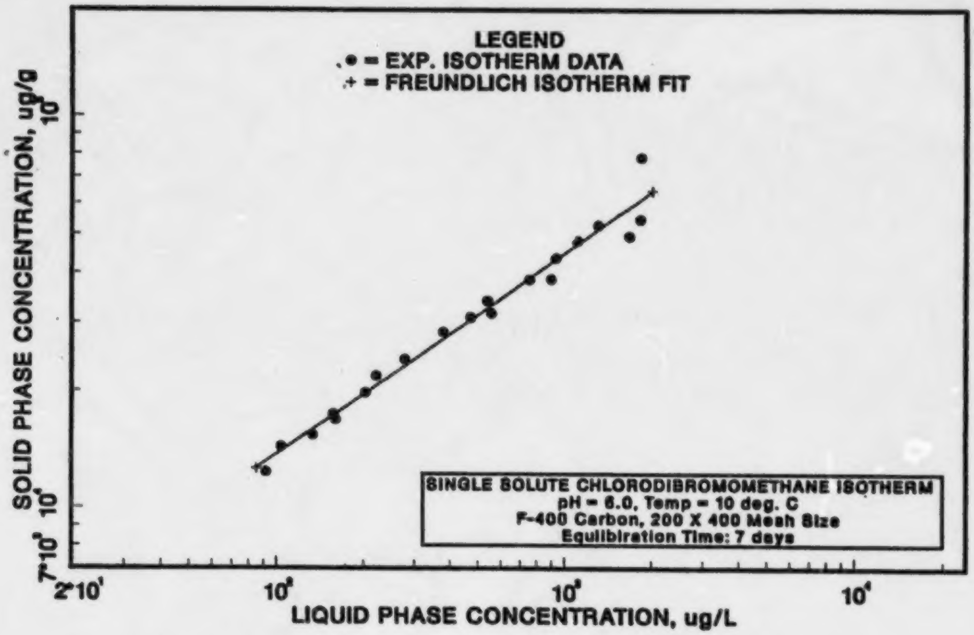

Figure II-17. Single Solute Isotherm Data and Freundlich Fit for Chlorodibromoethane on F-400 Carbon.

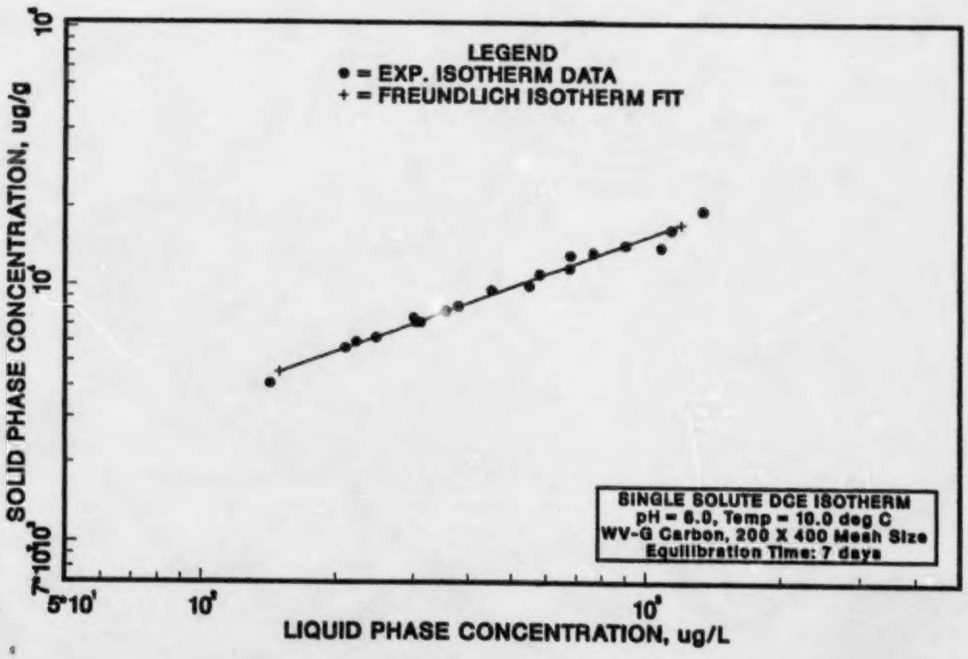

Figure II-18. Single Solute Isotherm Data and Freundlich Isotherm Fit for cis 1,2-Dichloroethene on WV-G Carbon.

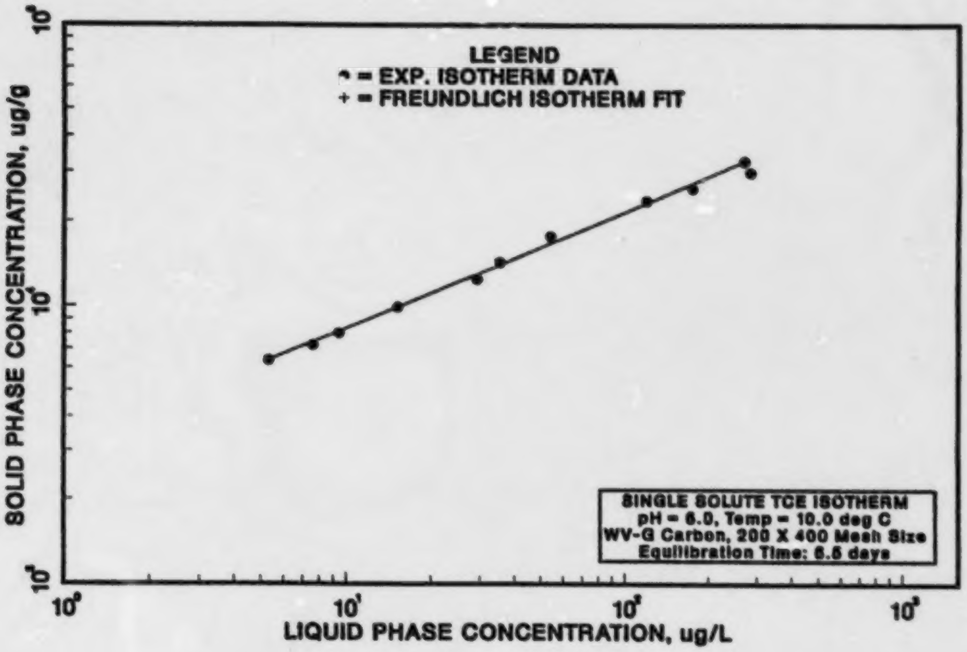

Figure II-19. Single Solute Isotherm Data and Freundlich Isotherm Fit for Trichloroethene on WV-G Carbon.

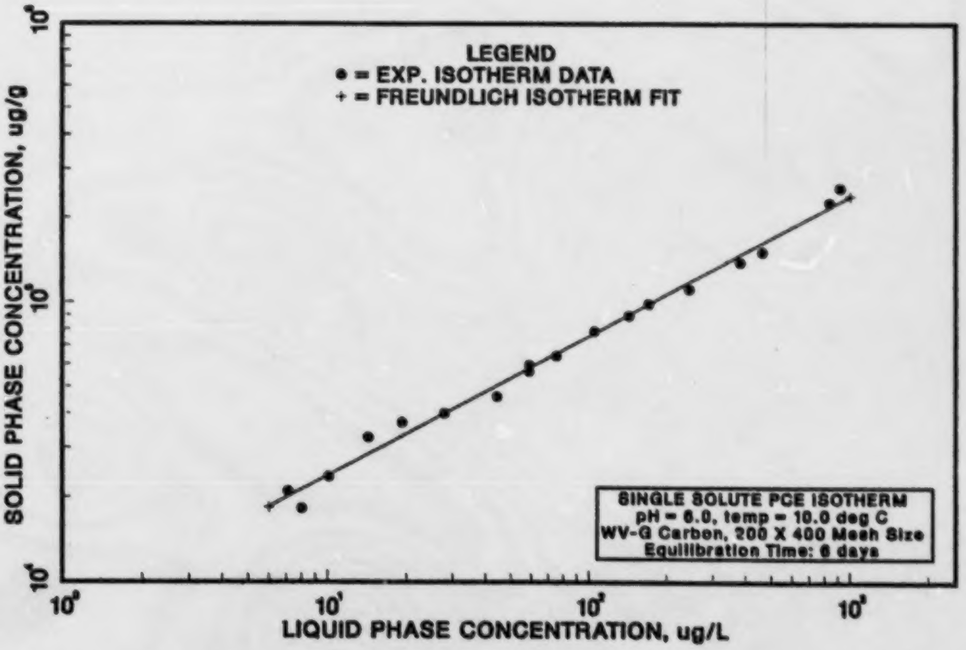

Figure II-20. Single Solute Isotherm Data and Freundlich Isotherm Fit for Tetrachloroethene on WV-G Carbon.

Table II-3. Single Solute Isotherm Parameters Used for Fixed Bed Modeling at 10°C to 16°C.

Compound	Date	K $(\mu m/g)(L/\mu m)^{(1/n)}$	1/n
Chloroform	10-1-84	30.4	0.5325
Cis 1,2-Dichloroethene	2-9-85	46.9	0.5562
Chlorodibromomethane	10-1-83	96.0	0.5170
1,2-Dibromoethane	10-1-83	118.4	0.4808
Bromoform	10-1-83	160.5	0.5629
Trichloroethene	2-6-85	191.7	0.4328
Tetrachloroethene	2-7-85	435.2	0.3847
Toluene	2-9-85	475.1	0.3282
Ethyl Benzene	2-16-85	714.4	0.2953
o-Xylene	2-16-85	894.6	0.2587
m-Xylene	2-10-85	1044.0	0.2458

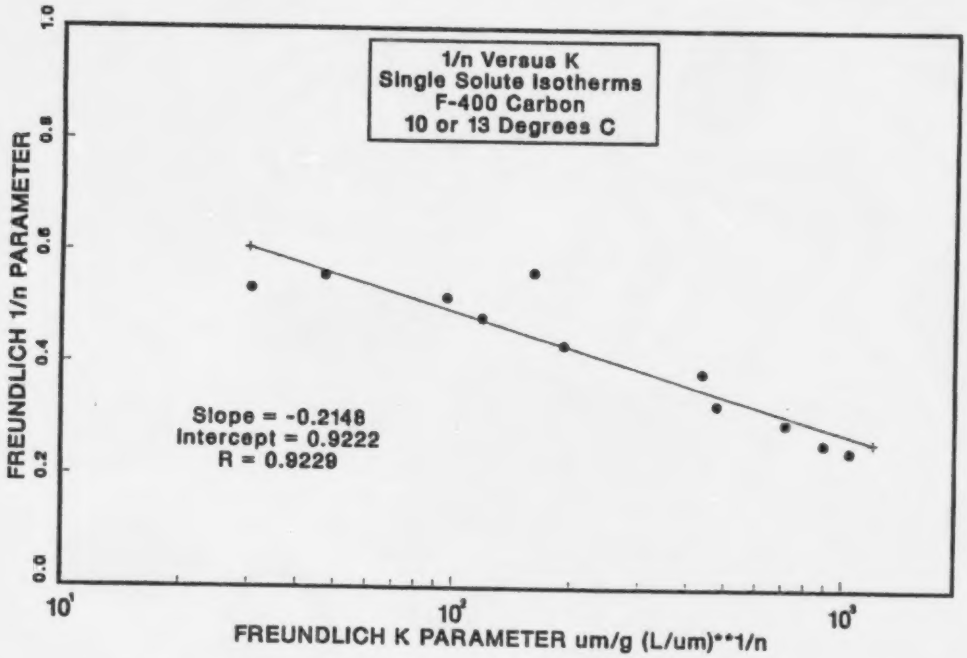

Figure II-21. Relationship Between 1/n and K for F-400 Carbon Isotherms at 10 or 13.8 Degrees Celsius.

Table II-4. Previously Reported Freundlich Isotherm Values.

Compound	Carbon Type	K	1/n	Conc. Range (ug/L)	Equilibration Time (days)	Temperature (^oC)	Reference
Trichloroethene	WV-W	92.8	0.5005	3 - 540	2.0	21	Ari (1982)
Trichloroethene	F-300	60.5	0.6200	5.5 - 300	.083	22	Dobbs and Cohen (1980)
Tetrachloroethene	F-300	112.0	0.5600	7.0 - 313	.083	22	Dobbs and Cohen (1980)

Units of K are $(umol/gm)(L/umol)^{1/n}$

1) The previously reported isotherms were conducted at much higher temperatures which yields lower capacities as shown in Figure II-2.

2) The parameters presented in Table II-4 were determined from isotherms that may not have been equilibrated for a long enough period of time.

3) The carbon used in this study is different from those shown in Table II-4.

4) The isotherms may have been completed over different concentration ranges.

III. PREDICTIVE MODELS FOR SINGLE SOLUTE ISOTHERMS

*Two very important predictive capabilities are the ability to predict single solute isotherms and the effect of temperature on single solute isotherms. The methods used in this thesis to predict single solute isotherms are Urano's modified Freundlich equation and the Polanyi adsorption potential theory. The methods used in this thesis to predict the effect of temperature on isotherms are Urano's modified Freundlich equation, the Clausius-Clapeyron equation, and the Polanyi adsorption potential theory. All of these techniques require the knowledge of solubilities of the compounds in question at the temperature of interest. Also, to predict the effect of temperature on isotherms, the solubility at the temperature of the reference isotherm is needed. Because solubilities found in reference sources are sometimes unreliable and are mainly found for only 25 degrees Celsius, predicting solubilities and the effect of temperature on solubilities must be addressed first. Following this will be sections dealing with predictions of single solute isotherms, and predictions of the effect of temperature on isotherms.

A. PREDICTING SOLUBILITIES OF HYDROPHOBIC COMPOUNDS

In the following section, the applicability of UNIFAC (Fredenslund, 1975) for determining solubilities for hydrophobic compounds in water is discussed.

1. Predicting Solubilities in Water using UNIFAC

UNIFAC is a group contribution method as defined by Fredenslund et al. (1975). The basic feature of UNIFAC is that it based on an extension of the quasi chemical theory of liquid mixtures (UNIQUAC). Abrams and Prausnitz (1975) showed that UNIQAUC gave good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolytes. UNIQUAC states that the logarithm of the activity coefficient is assumed to be the sum of two contributions. The first is a combinatorial part which is essentially due to differences in size and shape of the molecules in the mixture, and the second is a residual part, due to energy interactions. The combinatorial part is given by the athermal Flory-Huggins equation (Flory, 1965), and the residual part is defined by Wilson and Deal (1962). By knowing the functional groups of a compound and the UNIFAC parameters for these functional groups, the activity coefficient for the compound at infinite dilution in water can be found. From this, the solubility of the compound in water can be found from the following equation.

$$\text{Solubility} = 55.5 \ a_{org} / (\gamma_{aq}^{\infty})_{UNIFAC} \qquad \text{(III-1)}$$

Where, a_{org} is the activity of the organic in the liquid, and $(\gamma_{aq}^{\infty})_{UNIFAC}$ is the UNIFAC derived activity coefficient. The activity of the organic in the liquid is approximately one for hydrophobic compounds. Banerjee (1985) proposed that a more accurate prediction of the solubility can be obtained by the following empirical equation.

$$\log\ (\text{Solubility}) - 1.20 + 0.782 \log\ (a_{org} / (\gamma_{aq}^{\infty})_{UNIFAC}) \qquad \text{(III-2)}$$

By comparing well documented reference solubilities to the UNIFAC derived solubilities using the two above methods, it was found that Equation III-1 gave the best results for our data. Equation III-1 was therefore used instead of Equation III-2 for any modeling of data. Table III-1 contains the comparison between the UNIFAC derived solubilities and the range of reference solubilities at 25°C.

Table III-1. Comparison Between UNIFAC and Literature Solubilities.

	Solubility (mg/L) at 25°C			
Compound	UNIFAC Prediction Using Equation III-1	III-2	Reference Solubility	Average Reference and Standard Deviation
cis-1,2 dichloroethene	2332	3600	5934[2] 3500[1] 800[3*]	3411 ± 2568
trichloroethene[6]	1062	2081	1125[2] 1100[1] 1100[1] 1100[3] 1000[1]	1085 ± 49
tetrachloroethene[6]	428	1075	400[1] 225[2] 150[1*] 150[3] 140[1] 120[1*]	198 ± 105
toluene	423	937	680[2] 627[1] 578[5] 544[1] 534[1] 524[4] 520[1] 517[1] 515[1] 515[3*] 500[1]	550 ± 56
chloroform[6]	7672	9567	9300[3] 8200[1*] 8000[1*] 7950[1] 7900[1]	8270 ± 587
ethyl benzene	173	481	232[2] 208[1] 187[4] 177[1] 175[1] 161[1] 152[1] 131[1]	175 ± 31

Table III-1. (Continued)

	Solubility (mg/L) at 25°C			
Compound	Unifac Prediction Using Equation III-1	Unifac Prediction Using Equation III-2	Reference Solubility	Average Reference and Standard Deviation
m-xylene	104	324	196[1]	165
			173[1]	± 19
			171[2]	
			162[1]	
			160[4]	
			146[1]	
			134[1]	
o,p-xylene	104	324	287[2]	202
			221[4]	± 40
			213[1]	
			204[1]	
			175[1]	
			175[3*]	
			171[1]	
			167[1]	

[1] Mackay, D., Shiu, W.Y.,'A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest', J. Phys. Chem. Ref. Data, 10(4), 1981, 1175-1191.

[2] Perram, D.,Personal Communication,Michigan Technological Univ., Houghton, MI, 1985.

[3] Verschueren, K.,'Handbook of Environmental Data on Organic Chemicals', Van Nostrand Reinhold, New York, 2nd Edition, 1983.

[4] Banerjee, S.,'Solubility of Organic Mixtures in Water', Environ. Sci. Technol., 18(8), 1984, 587-591.

[5] Miller, M.M., Wasik S.P., Huang G.L., Shiu W.Y., Mackay, D.,'Relationship Between Octanol-Water Partition Coefficient and Aqueous Solubility',Environ. Sci. Technol., 19(6), 1985, 522-529.

[6] Munz and Roberts (1986) report the ranges of solubilities for TCE, PCE, and chloroform to be 700-2640 mg/L, 87-206 mg/L, and 6650-8200 mg/L, respectively.

Munz and Roberts (1986) conclude that UNIFAC does a good job in calculating solubilities of hydrophobic compounds, but it does not predict the effect of temperature very well. They give no indication of whether UNIFAC is more accurate at a specific temperature, but only say that experimentally determined solubilities decrease slightly with temperature while UNIFAC derived solubilities increase with temperature. It must be noted that experimentally determined solubilities as shown in Table III-1 have a tremendous amount of scatter even at the same temperature. Contrary to what Munz and Roberts have found, Shinoda (1978) states that the solubility of liquids should increase with increasing temperature which is what UNIFAC predicts. A computer program of the UNIFAC method can be found in Appendix V.

B. PREDICTING SINGLE SOLUTE ISOTHERMS

Predictive methods for determining isotherm parameters are needed given the scarcity of reliable data on organic compounds. Two different methods which can be used to predict single solute isotherms are Urano's modified Freundlich equation, and the Polanyi potential theory. These methods are discussed in the following sections.

1. Correlating Single Solute Isotherms Using Urano's Modified Freundlich Equation.

The basic idea for the use of a modified Freundlich equation is to obtain a characteristic isotherm by plotting the solid-phase concentration as some function of liquid-phase concentration. According to Roginsky (1949), the molar adsorbed amount Q can be obtained in the form of a modified Freundlich equation by integration of the distribution function of the adsorption potential, $f(\varepsilon)$.

$$Q = \int_{\varepsilon_{eq}}^{\varepsilon_{max}} f(\varepsilon)\, d\varepsilon \qquad \text{(III-3)}$$

Where, ε is the molar adsorption potential, within the limits of the equilibrium potential ε_{eq} and the maximum potential ε_{max}. Adamson (1976) writes the distribution function as an exponential function.

$$f(\varepsilon) = A \exp(-a\ \varepsilon) \qquad \text{(III-4)}$$

Therefore,

$$Q = \int_{\varepsilon_{eq}}^{\varepsilon_{max}} A \exp(-a\ \varepsilon)\, d\varepsilon \qquad \text{(III-5)}$$

Integrating,

$$Q = -(A/a)\ (\exp(-a\ \varepsilon_{max}) - \exp(-a\ \varepsilon_{eq})) \qquad \text{(III-6)}$$

ε_{max} is the adsorption potential in a infinitely dilute solution and can be approximated by infinity. Therefore,

$$Q = (A/a)\ \exp(-a\ \varepsilon_{eq}) \qquad \text{(III-7)}$$

To complete the modification of the Freundlich Equation, ε_{eq} must be found.

Polanyi proposed that his potential theory for the adsorption of vapor could be applied to the adsorption from solution, and the molar potential of adsorption from solution at the equilibrium concentration C could be expressed by:

$$\varepsilon_{eq} = RT \ln(C_s/C) \qquad \text{(III-8)}$$

in which, R is the gas constant, T is the absolute temperature, C_s is the solubility, and C is the bulk phase concentration of solute. Using this in Equation III-7,

$$Q = (A/a) \exp(aRT \ln(C_s/C)) \qquad \text{(III-8)}$$

or,

$$Q = (A/a)\ (C/C_s)^{(aRT)} \qquad \text{(III-10)}$$

or,

$$Q = \frac{A}{a\ C_s^{(aRT)}}\ C^{(aRT)} \qquad \text{(III-11)}$$

Equation III-11 is comparable to the Freundlich Equation. Where,

$$K = \frac{A}{a\ C_s^{(aRT)}} \qquad \text{(III-12)}$$

and

$$1/n = aRT \qquad \text{(III-13)}$$

The modified Freundlich equation is obtained by letting $k'=A/a$. Where k' is the limiting adsorbed amount at the saturation concentration. Therefore, substituting Equations III-12 and III-13 into III-11,

$$Q = k'\ (C/C_s)^{(1/n)} \qquad \text{(III-14)}$$

Urano et al. (1980) stated that the term 'A' should be constant for a given adsorbent, and the term 'a' should be constant for a homologous series of compounds. Because Equation III-13 relates 1/n to 'a', the homologous series would be defined by compounds which have identical 1/n values. This assumes that the reduced concentrations are equal.

Traube's Rule states that when the molar concentration adsorbed is plotted versus the liquid-phase concentration divided by the solubility, the isotherm lines should superimpose onto each other for compounds of like structure. Hansen and Craig (1954) found that this was the case for fatty acids in aqueous solution on activated carbons. Urano _et al_. (1980) found that this was only an approximate relationship for a number of compounds. Figures III-1 and III-2 show Traubes Rule applied to the isotherms obtained at Michigan Technological University for halogenated and aromatic compounds respectively. An approximate relationship is found in both cases.

The modified Freundlich equation may describe this approximate relationship. As stated before, the value of 'a' varies from compound to compound because 1/n varies. However, 1/n values are roughly equal for structurally similar compounds. This may explain why like compounds show an approximate relationship when plotted as Traube's rule.

To look into the development more fully, Equation III-12 was studied to see if the constant 'A' is independent of the solute. If it is, $1/a\ C_s^{-aRT}$ plotted against K will result in a straight line with a slope of 1/A. The value of 'a' for each point was calculated from Equation III-13 using the Freundlich 1/n values obtained from a single solute isotherm. Figure III-3 shows the resultant plot for the research completed at Michigan Technological University. The figure shows that

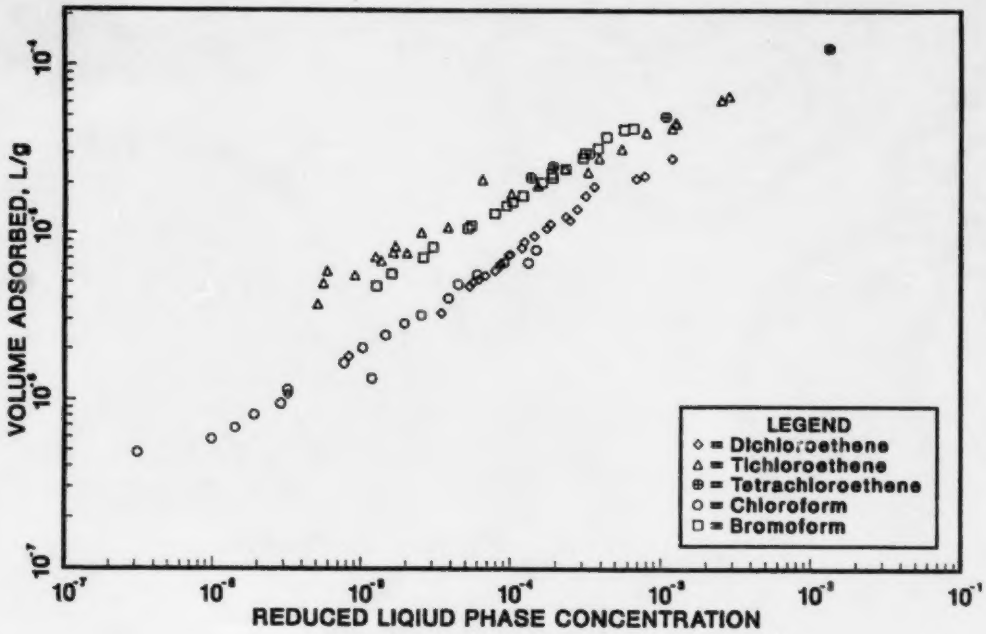

Figure III-1. Traubes Rule Applied to F-400 Carbon Isotherms of Halogenated Compounds.

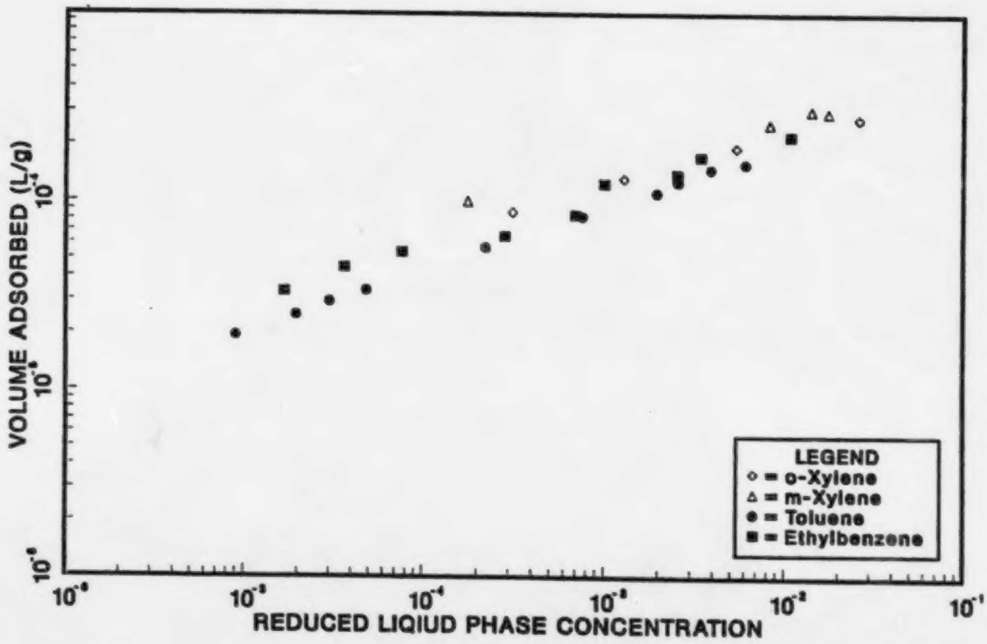

Figure III-2. Traubes Rule Applied to F-400 Carbon Isotherms of Aromatic Compounds.

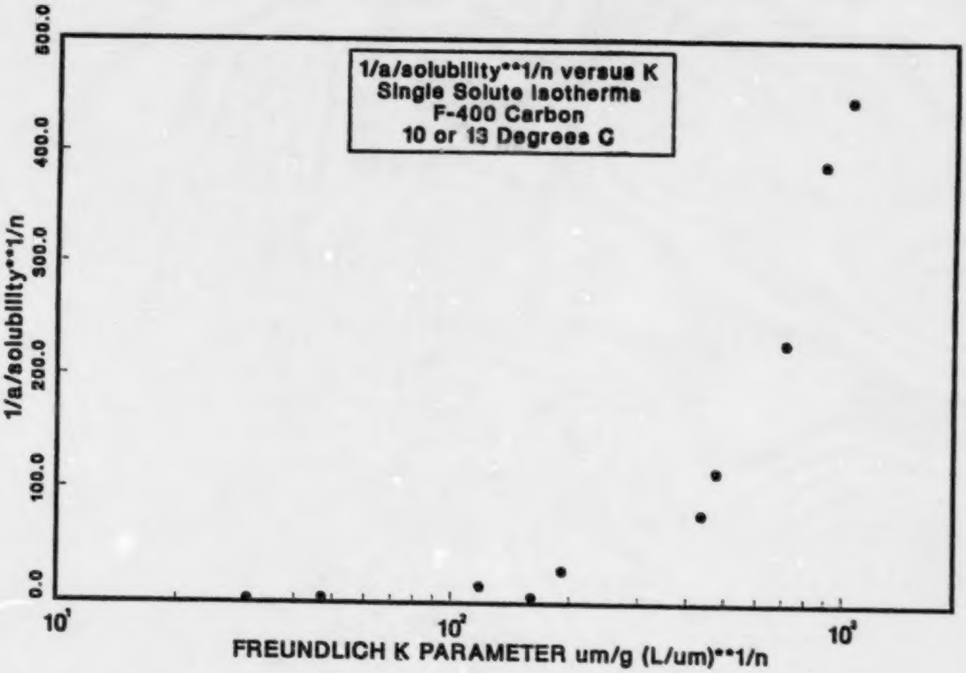

Figure III-3. Application Testing of the Modified Freundlich Equation as Defined by Urano.

'A' is not independent of the compound because of the increase in slope with K. This means that the practicality of the modified Freundlich equation to predict single solute isotherms is not present.

2. Correlating Single Solute Isotherms Using the Polanyi Adsorption Potential Theory

In this discussion, it will be shown that the Polanyi adsorption potential theory can be used to correlate single solute isotherm data of hydrophobic compounds. From this correlation, good estimates of Freundlich isotherm parameters can be calculated. The compounds used in the correlation are halogenated aliphatics and aromatics. Once the limitations of the correlation have been established, the isotherms of many hydrophobic compounds can be predicted from the isotherm of a reference compound and the solubility and molar volume of the compound of interest.

The Polanyi potential theory has been applied to the adsorption of gases and mixed vapors (Grant, R.J., Manes, M., Smith S.B., 1962)(Grant, R.J., Manes, M., 1964)(Grant R.J., Manes, M., 1966)(Rick, B., 1986), and of solutes using solvents other than water (Manes, M., Hofer, L.J., 1969). Also, Arbuckle (1981) has correlated the aqueous phase adsorption of a series of alcohols, aldehydes, and ketones using the Polanyi theory. Consequently, the Polanyi theory has been generally useful in correlating and predicting isotherm data even though it is a semi-empirical thermodynamic model.

a. Background

The Polanyi theory assumes that there is a fixed volume which is close to the adsorbing surface where adsorption occurs. Polanyi (1920) defines the adsorption potential (ε_{eq}) as the work which is needed to move any molecule from the bulk solution to the adsorption space.

$$\varepsilon_{eq} = RT \ln(C_s/C) \qquad \text{(III-15)}$$

in which, R is the ideal gas constant; T is the temperature; C_s is the solubility of the solute; and C is the liquid phase concentration.

It is assumed that ε_{eq} varies from a maximum value close to the surface with low bulk solution concentrations to zero when the pores are filled and the solubility limit is reached in the bulk solution. This can be represented as a series of equipotential surfaces which define separate adsorption spaces as shown in Figure III-4. Accordingly, the solute occupies the adsorption spaces closest to the carbon up to some equipotential surface. By plotting the cumulative adsorbed volume versus ε_{eq}, the 'characteristic curve' is obtained (Lewis, 1950). By plotting the volume adsorbed versus the adsorption potential divided by a normalizing physical property which accounts for the major cause for adsorption, gas phase characteristic curves for many compounds will coincide. Normalizing properties suggested by previous researchers include molar volume, polarizability, or parachor (Reucroft et al., 1971). The correlation can therefore be described by Equation III-16 with ω equaling one if the data falls on a straight line

$$\ln W = B\,(\varepsilon_{eq}/N)^{\omega} + \ln W_o \qquad \text{(III-16)}$$

in which, W is the volume adsorbed; B and ω are empirical constants; N is the correlating factor, and W_o is the maximum volume adsorbed, or the y-intercept.

If polarizabilities are being used as the correlating factor and they are not available in literature, they can be calculated by the

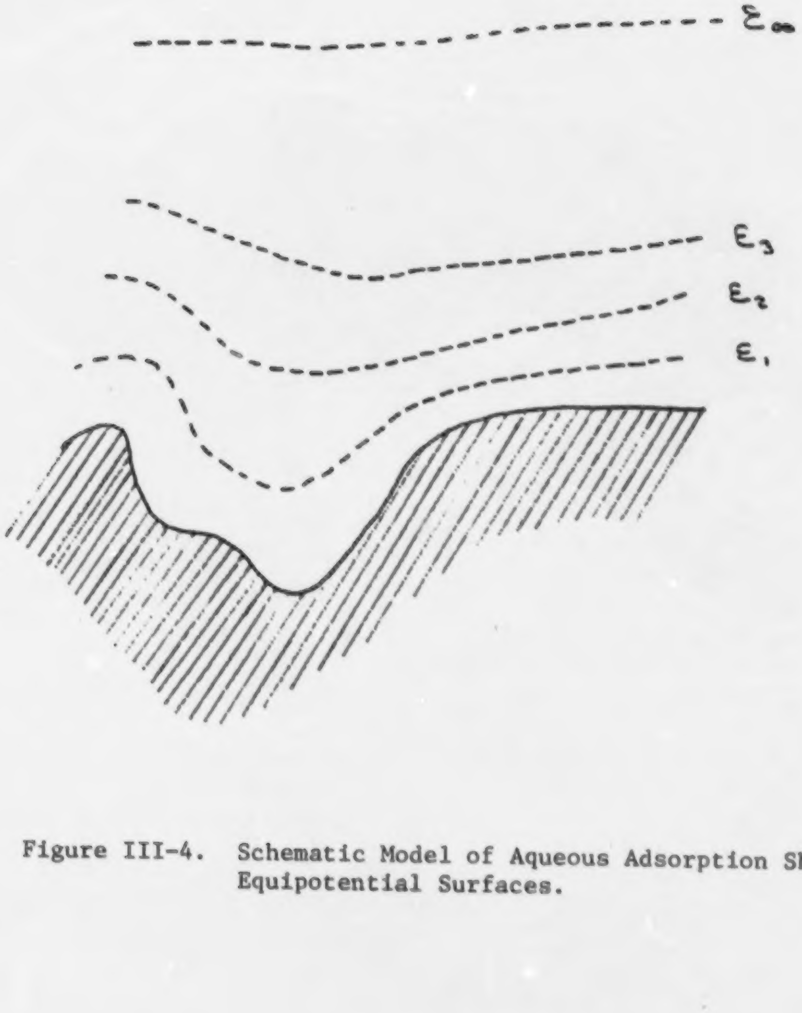
ε_∞
ε_3
ε_2
ε_1

Figure III-4. Schematic Model of Aqueous Adsorption Showing Equipotential Surfaces.

Lorenz-Lorentz equation (Perry, 1973).

$$\alpha_i = (\eta_i^2 - 1)/(\eta_i^2 + 2)\ V_i \qquad \text{(III-17)}$$

in which, η is the refractive index; and V is the molar volume.

Parachor can be found from the Sugden equation (Perry, 1973).

$$P = \sigma^{1/4}\ V \qquad \text{(III-18)}$$

in which, σ is the surface tension, and V is the molar volume. It can also be calculated using a structural contribution method (Perry, 1973).

Manes and Hofer (1969) reported an improvement in correlating their aqueous phase data to gas phase data by fitting the refractive index of water, η_w, in the following normalizing factor.

$$\lambda = \alpha_s - (\eta_w^2 - 1)/(\eta_w^2 + 2)\ V_s \qquad \text{(III-19)}$$

in which, s refers to the solute; and w refers to the solvent, water.

b. Results

Isotherms which were conducted on F-400 and WV-G carbons are listed on Table III-2 along with the solubilities, densities, refractive indices, and parachor of the solutes. Figure III-5 shows F-400 carbon isotherms plotted as volume adsorbed versus adsorption potential divided by molar volume. The data essentially falls on a straight line with a slight curvature at low adsorption potentials. The best fit of the data using Equation III-16 is also shown in Figure III-5. The WV-G carbon isotherms are plotted as a correlation curve in Figure III-6. No curvature is evident for the WV-G carbon because only a limited range of data was available, consequently, it was fit with a straight line.

Table III-2. Physical Properties of the Compounds Used in the Polanyi Correlation Curve.

Compound	Isotherm Temperature °C	UNIFAC Derived Solubilities (mg/L)	Density (g/ml)	Refractive Index[1]	Parachor[2] $(dyne/cm)^{0.25}*cm^3/gmol$
cis 1,2-dichloroethene	10.0 13.8	1921.0 2021.0	1.280	1.445	178.2
trichloroethene	10.0 13.8	836.0 890.6	1.462	1.475	217.8
tetrachloroethene	10.0 13.8	322.1 347.0	1.620	1.504	257.4
toluene	13.8	360.5	0.867	1.496	245.4
ethylbenzene	13.8	145.3	0.867	1.496	285.4
o,p-xylene	13.8	86.5	0.870	1.500	285.4
m-xylene	13.8	86.5	0.864	1.497	285.4
chloroform	10.0	6459.4	1.446	1.446	189.6
bromoform	10.0	3033.0[3]	2.890	1.598	231.6
1,2-dibromoethane	10.0	1696.0[3]	2.179	1.587	256.2

[1] CRC,'Handbook of Chemistry and Physics',62nd Edition, CRC Press,Inc. Boca Raton, Florida,1981,C-318.

[2] Calculated from structural contributions. Perry, R.H., Chilton, C.H.,'Chemical Engineers Handbook', 5th edition, New York, 1973, 3-227.

[3] Mackay,D.,Shiu, W.Y., J.Phys. Chem. Ref. Data, 1981, 10(4), 1175-1191.

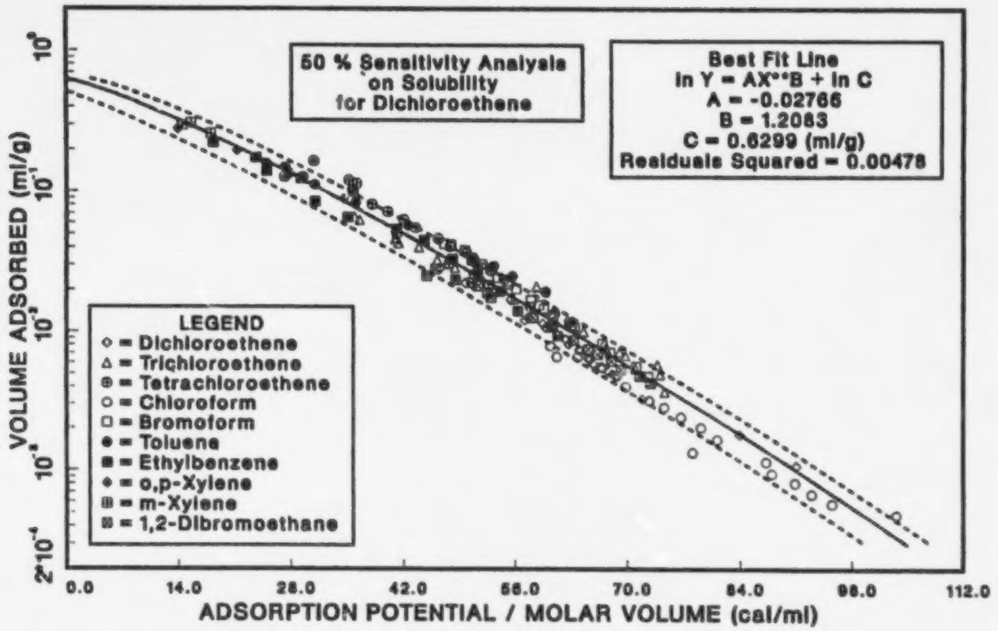

Figure III-5. Polanyi Potential Correlation Curve for F-400 Carbon Isotherms Using Molar Volume as the Normalizing Factor and UNIFAC Derived Solubilities.

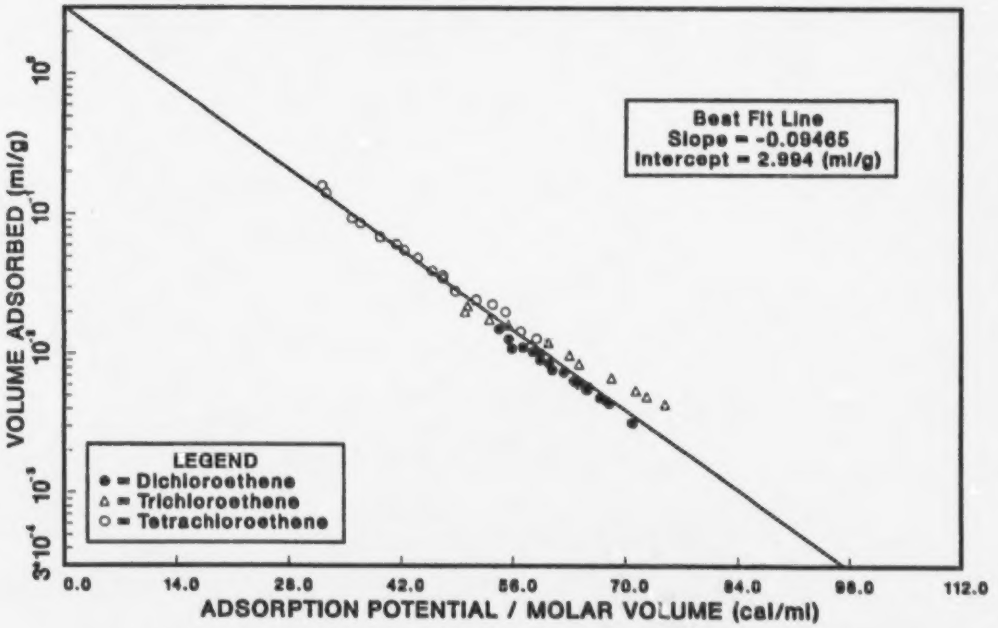

Figure III-6. Polanyi Potential Correlation Curve for WV-G Carbon Isotherms Using Molar Volume as the Normalizing Factor and UNIFAC Derived Solubilities.

When polarizability is used for the normalizing factor, as shown in Figure III-7, the data diverges for the brominated compounds. As shown in Table III-2, it is interesting to note that the brominated compounds have the largest refractive indices. Figure III-8 shows the correlation plot using parachor as the normalizing factor. Whereas, the data correlated well, it was found that the correlation curve using molar volume as the normalizing factor correlated better.

If Equation III-19 is used as the normalizing factor, as shown in Figure III-9, the brominated compounds show the same divergence as when polarizability was used as the normalizing factor. This is expected because of the similarities between correlating factors.

To calculate the data for the correlation plot, the solubilities of the compounds were calculated using the group contribution method, UNIFAC, which is described by Fredenslund et al. (1975). UNIFAC was used because reference solubilities for the compounds of interest did not give consistent values, and they were not at the temperature of the isotherms. It must be noted however, that the UNIFAC parameters are not complete for compounds which contain bromine. Therefore, the correlation curve for the bromine containing compounds were calculated using MacKay's data at 25°C (MacKay, 1981). The scatter in the correlation curve is expected to be greater than the error in using the 25°C solubilities for the brominated compounds.

To test the Polanyi Theory, the Freundlich K and 1/n values were back-calculated from the correlation curve. The results shown in Table III-3 and Table III-4 demonstrate that if the data is fit by Equation III-16, a good approximation of the Freundlich parameters can be obtained from the Polanyi correlation. It is important to recognize

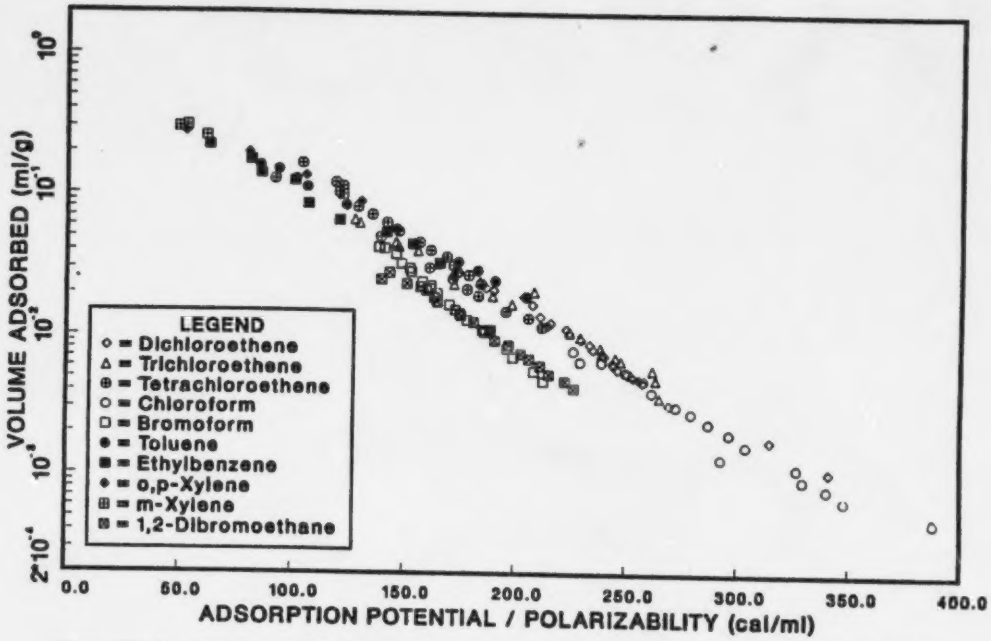

Figure III-7. Polanyi Potential Correlation Curve for F-400 Carbon Isotherms Using Polarizability as the Normalizing Factor and UNIFAC Derived Solubilities.

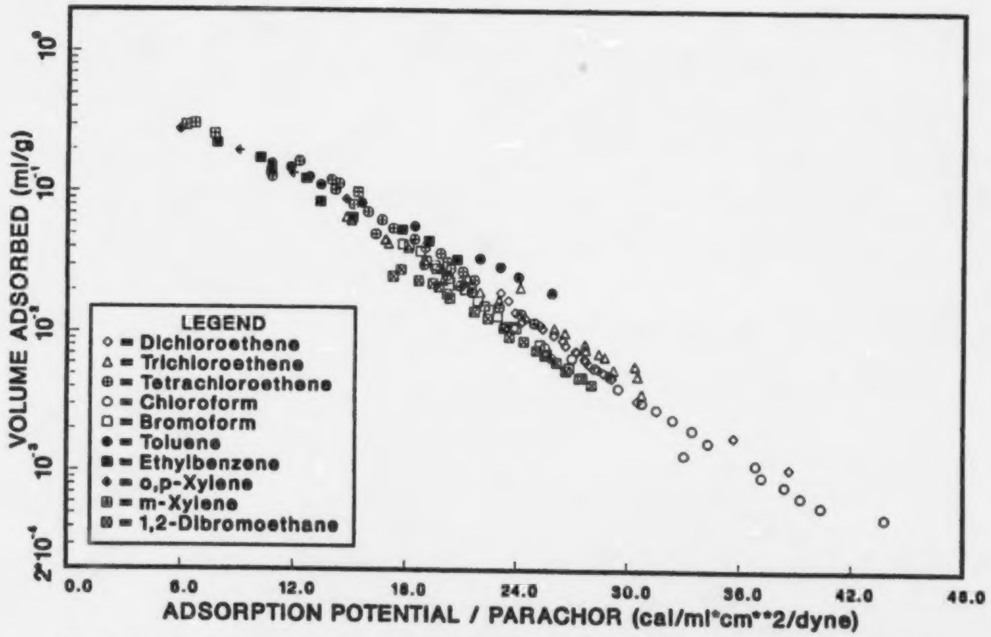

Figure III-8. Polanyi Potential Correlation Curve for F-400 Carbon Isotherms Using Parachor as the Normalizing Factor and UNIFAC Derived Solubilities.

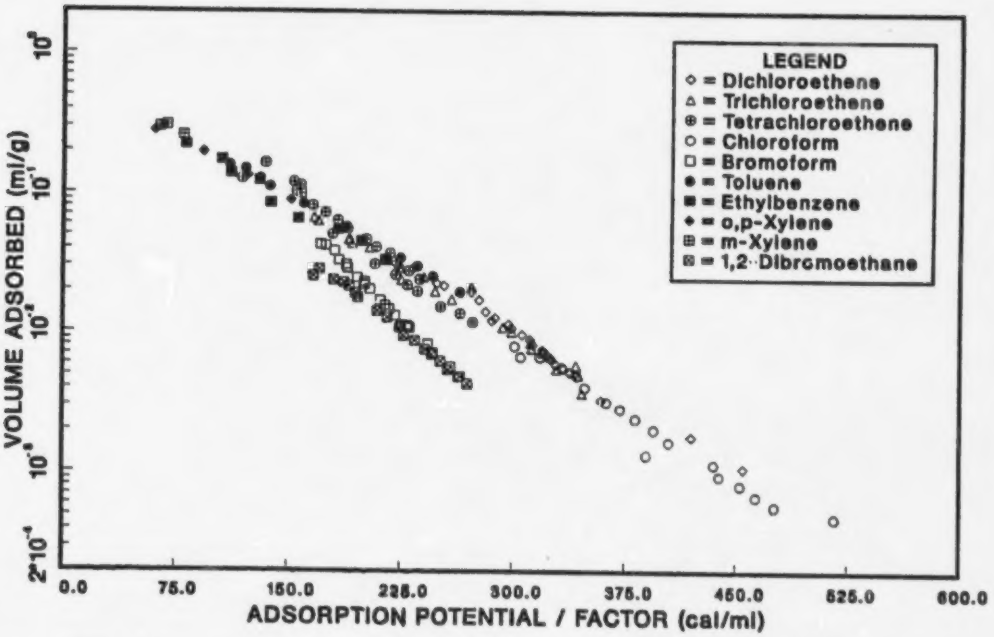

Figure III-9. Polanyi Potential Correlation Curve for F-400 Carbon Isotherms Using a Normalizing Factor as Defined by Manes et al. and UNIFAC Derived Solubilities.

Table III-3. Predictions of Freundlich Isotherm Parameters from the Correlation Curve as Compared to Experimental Value for F-400 Carbon Isotherms.

	$K\ (\mathrm{um/g})(\mathrm{L/um})^{1/n}$			$1/n$		
Compound	Experimental	Predicted	% Error	Experimental	Predicted	% Error
chloroform	30.4	40.9	34.7	0.5325	0.5756	-8.09
cis 1,2-dichloroethene	46.9	48.4	3.20	0.5562	0.6047	8.72
1,2-dibromoethane	118.4	152.0	28.4	0.4808	0.5064	5.32
bromoform	160.5	135.8	-15.4	0.5629	0.5148	8.55
trichloroethene	191.7	186.1	2.92	0.4328	0.4857	12.2
toluene	475.1	376.9	-20.7	0.3282	0.3901	18.9
tetrachloroethene	435.2	452.2	3.90	0.3847	0.4069	5.77
ethylbenzene	714.4	706.2	-1.15	0.2953	0.3211	8.74
o,p-xylene	894.6	862.1	-3.63	0.2587	0.3026	17.0
m-xylene	1044.0	865.2	-17.1	0.2458	0.3013	22.6
		Average |% Error| = 13.1			Average |% Error| = 11.6	

Table III-4. Predictions of Freundlich Isotherm Parameters from the Correlation Curve as Compared to Experimental Value for WV-G Carbon Isotherms.

	K $(\mathrm{um/g})(\mathrm{L/um})^{1/n}$			1/n		
Compound	Experimental	Predicted	% Error	Experimental	Predicted	% Error
chloroform		28.5			0.6447	
cis 1,2-dichloroethene	35.4	37.7	6.50	0.6441	0.7028	9.11
1,2-dibromoethane		125.7			0.6172	
bromoform		104.4			0.6167	
trichloroethene	181.0	185.5	2.49	0.4073	0.5927	45.5
toluene		423.3			0.5075	
tetrachloroethene	589.5	570.6	3.21	0.5017	0.5199	3.63
ethylbenzene		1015.9			0.4405	
o,p-xylene		1441.6			0.4229	
m-xylene		1459.9			0.4199	
	Average $\|\%\ \mathrm{Error}\| = 4.07$			Average $\|\%\ \mathrm{Error}\| = 19.4$		

that the Freundlich K and 1/n depend on the relative concentration; consequently, the appropriate range must be used to estimate K and 1/n. A computer program which determines Freundlich K's and 1/n's from a correlation curve can be seen in Appendix VI.

Because of the uncertainty in solubilities, a plus and minus 50 percent sensitivity analysis on solubility was conducted for DCE. The resultant bounds are shown in Figure III-5. This figure demonstrates that the correlation curve is fairly sensitive to solubilities, and the solubility only affects the intercept of the correlation curve as shown in Equation III-16.

3. Comparison of Methods Used to Correlate Single Solute Isotherms

The results of the work completed for Urano's modified Freundlich equation demonstrates that it can not be used as a correlating model for isotherms. The equation does seem to predict the pattern of Traube's Rule where similar compounds have modified isotherms which roughly superimpose on each other. This however, does not give the procedure predictive capabilities.

Isotherm data for hydrophobic compounds were correlated by Polanyi adsorption potential theory. This correlation appears to be able to predict single solute Freundlich isotherm parameters for other hydrophobic compounds knowing only the density and solubility of the solute. A 50 percent sensitivity analysis on the effect of the solubility showed that the correlation curve was somewhat sensitive to solubilities. The normalizing factors: polarizability, parachor, and that which was proposed by Manes and Hofer (1969), did not correlate the data as well as the molar volume.

C. PREDICTING THE EFFECT OF TEMPERATURE ON ISOTHERMS

It is important to be able to predict the effect of temperature on isotherms. Three methods which were studied are Urano's modified Freundlich equation, the Clausius-Clapeyron equation, and the Polanyi adsorption potential theory.

1. Predicting the Effect of Temperature Upon Isotherms Using Urano's Modified Freundlich Equation

Even though the Modified Freundlich Equation is not practical for predicting single solute isotherms of different compounds, it still may be useful to predict the effect of temperature on a isotherm of a specific compound. The modified Freundlich equation is defined by Equations III-20 and III-21 as stated earlier.

$$K= A/(a\ C_s^{(aRT)}) \qquad \text{(III-20)}$$

and

$$1/n = aRT \qquad \text{(III-21)}$$

It can be seen that by using Equation III-21, the constant 'a' can be calculated using the value of 1/n from the reference isotherm. The Freundlich K of the reference isotherm can be used with the constant 'a' in Equation III-20 to solve for the constant 'A'. If the constants 'a' and 'A' are independent of temperature, they can be used to calculate the K and 1/n for a isotherm at a different temperature. This is only possible if the solubility of the compound is known at the temperatures of the reference isotherm and that of the predicted isotherm. The results of this method for TCE and chloroform are shown in Figures III-10 and III-11, respectively. As can be seen in these two figures, the isotherm shift due to the effect of temperature is predicted to be approximately one-half of what was expected from the

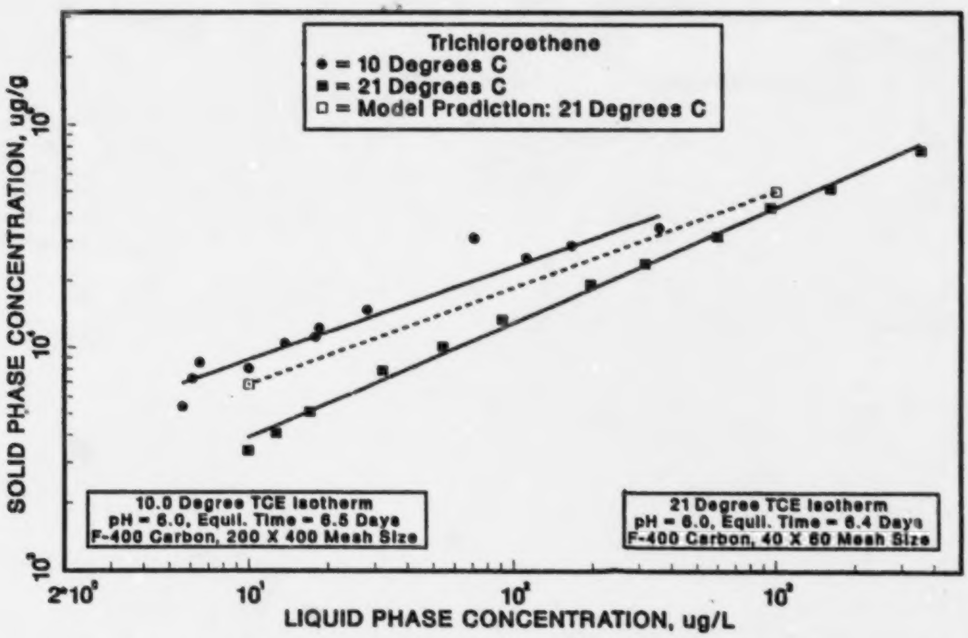

Figure III-10. Predicting the Effect of Temperature on the Isotherm of Trichloroethene Using the Modified Freundlich Equation as Defined by Urano.

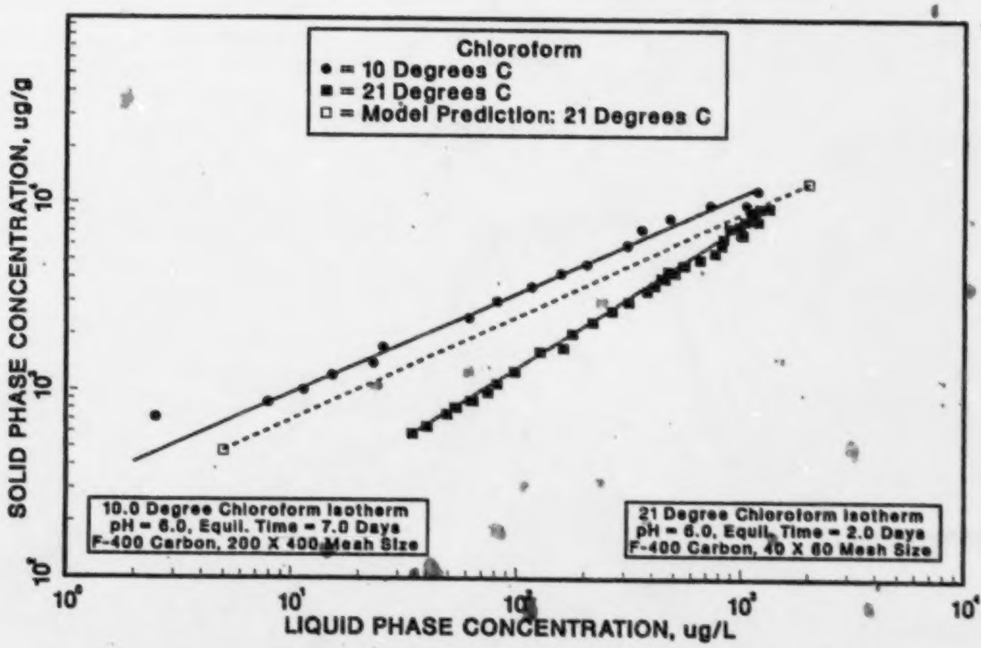

Figure III-11. Predicting the Effect of Temperature on the Isotherm of Chloroform Using the Modified Freundlich Equation as Defined by Urano.

experimental data.

2. Predicting the Effects of Temperature Upon Isotherms Using the Clausius-Clapeyron Equation

Another method of determining the effect of temperature on isotherms starts with the Clausius-Clapeyon Equation (Urano, 1981). The complete derivation and corresponding computer program can be seen in Appendix VII. The Clausius-Clapeyron equation is:

$$Q_{iso} = RT^2 \ (\partial \ln C/\partial T)_q \qquad \text{(III-22)}$$

in which, C is the liquid-phase concentration, T is the absolute temperature, R is the gas constant, Q_{iso} is the isosteric heat of adsorption, and q is the solid-phase concentration. If it is integrated assuming constant q and Q_{iso}, and solved for C_2, the following equation is obtained.

$$C_2 = C_1 \exp((1/T_1 - 1/T_2)\ Q_{iso}/R) \qquad \text{(III-23)}$$

The only unknown in predicting a liquid-phase concentration at a different temperature is Q_{iso}. It must be solved in terms of known variables. This is completed using the following equation which defines the isosteric heat of adsorption as the adsorption potential minus the heat of dissolution of the adsorbate into solution.

$$Q_{iso} = RT \ln (C_s/C) + RT^2 \ d \ln Cs/dT \qquad \text{(III-24)}$$

The results of this method are shown in Figures III-12 and III-13 for TCE and chloroform, respectively. The results are similar to those found using the modified Freundlich equation, where the isotherm prediction lies roughly half the distance between 10°C reference isotherm and the 21°C isotherm which was to be predicted.

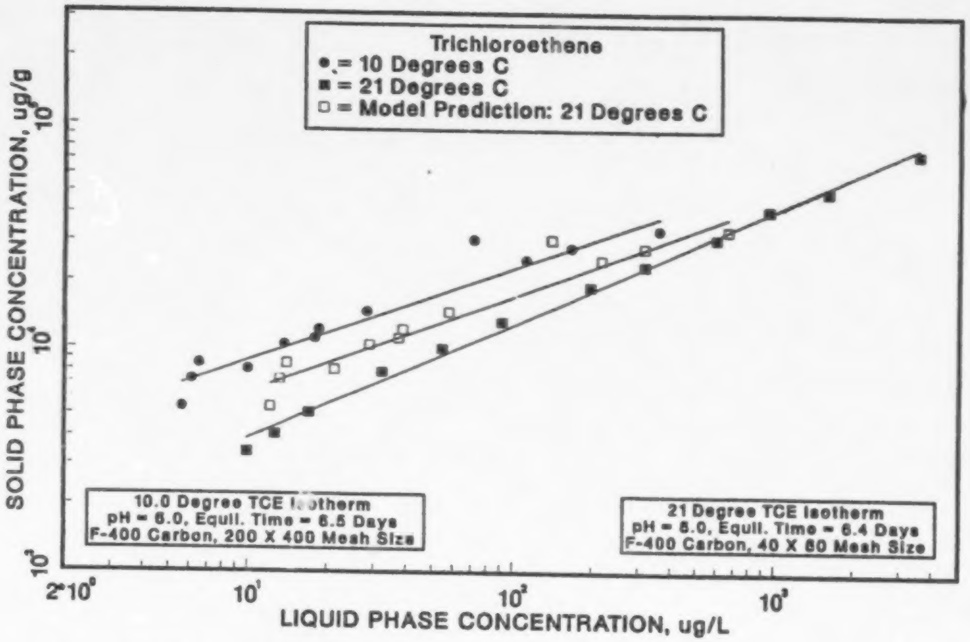

Figure III-12. Predicting the Effect of Temperature on the Isotherm of Trichloroethene Using the Clausius-Clapeyron Equation.

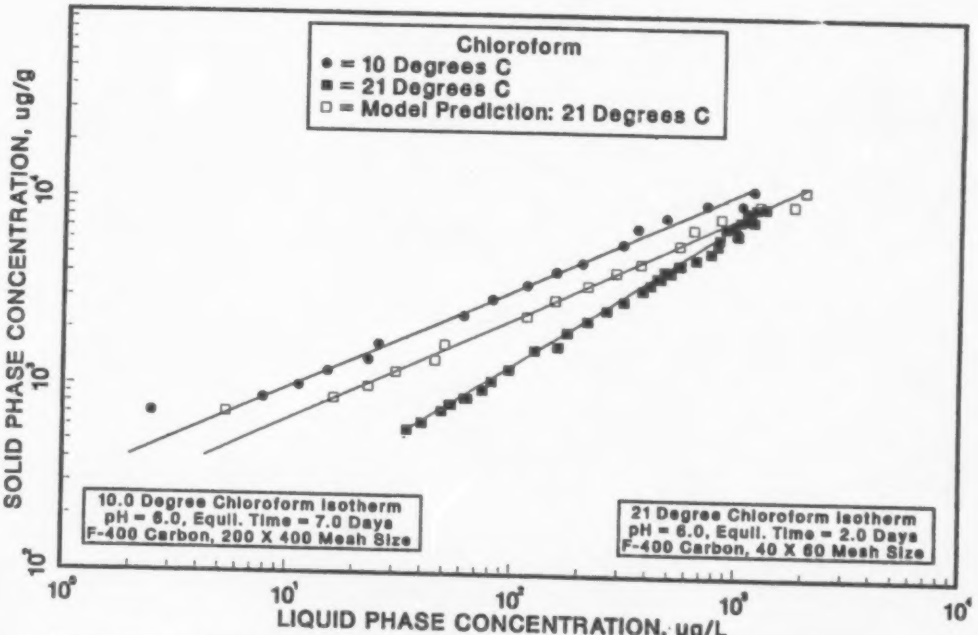

Figure III-13. Predicting the Effect of Temperature on the Isotherm of Chloroform Using the Clausius-Clapeyron Equation.

3. Predicting the Effect of Temperature on Isotherms Using the Polanyi Adsorption Potential Theory

Polanyi has proposed that the correlation curve of volume adsorbed versus adsorption potential divided by a normalizing factor is independent of temperature. This was confirmed by Itaya et al. (1984). The predictions for the effect of temperature on the TCE and chloroform isotherms were found to be the same as using Urano's modified Freundlich equation shown in Figures III-10 and III-11.

4. Comparison of Methods Used to Determine the Effect of Temperature on Isotherms

Urano's modified Freundlich equation, the Clausius-Clapeyron equation, and the Polanyi potential theory give essentially the same prediction for the effect of temperature on isotherms. As seen in Appendix VII, one of the assumptions for predicting the effect of temperature on isotherms using the Clausius-Clapeyron equation is to assume that the modified Freundlich constants 'A' and 'a' are independent of temperature. Because this is the assumption in using Urano's modified Freundlich equation to predict the effect of temperature on isotherms, it would seem that Urano's further derivation of the method using the Clausius-Clapeyron equation is not needed. Also, Urano's modified Freundlich method gives the same prediction of the effect of temperature as the Polanyi potential method. Therefore, any further work in predicting the effect of temperature on isotherms requires only one method. It is suggested that the Polanyi potential theory be used because it is well known and it can correlate single solute isotherms.

Since all three predictive methods predict the higher temperature isotherm in the same manner, the question comes up if the two isotherms used for predictions are correct. A difference between the two isotherms is that the 21°C isotherm was completed on larger sized carbon. This difference would not seem to cause any error because both isotherms were run to equilibrium. Another difference is that the isotherms, although they were completed on the same carbon, they were taken from different shipments of carbon and this could cause some deviations in the results. These deviations are expected to be small, however.

Upon looking at other isotherms which were completed at Michigan Technological University, the 13.8°C isotherms were determined to be so close to the 10°C isotherms that the difference was indistinguishable. This would be predicted by the three models discussed, but not by the difference expected by noticing how far the 21°C isotherm is from the 10°C isotherm. This seems to suggest that possibly the 21°C isotherm is displaced from the 10°C isotherm an inordinate amount.

IV. MULTICOMPONENT EQUILIBRIUM STUDIES

The occurrence of multiple SOCs present in contaminated groundwater is common (U.S. EPA, 1984). Therefore, it is necessary to be able to predict multicomponent adsorption. The use of ideal adsorbed solution theory (IAST) is one way in which this can be handled. IAST requires that all the adsorbing components present in the water be identified and their single solute isotherms be known. In the Wausau water, it was determined that there are seven VOCs present in the water that have a high concentrations and adsorb to a significant amount. Therefore, IAST was used to predict competitive interactions between these seven VOCs, while ignoring the total organic carbon (TOC) background.

Since it is an almost impossible task to identify all adsorbing species present in a contaminated drinking water, the use of hypothetical components will be evaluated. Hypothetical components can be used to represent the unknown portion of compounds present in the groundwater. The hypothetical component Freundlich isotherm parameters can be determined by fitting a raw water isotherm for a single component, or by fitting a TOC isotherm.

A. COMPARISON BETWEEN SINGLE SOLUTE ISOTHERMS AND ISOTHERMS CONDUCTED WITH WAUSAU WATER

In order to determine whether competitive interactions occur between the background components in the Wausau water and DCE, TCE, and PCE, isotherms were conducted with these compounds using the same procedures presented in Appendix III for the organic-free water isotherms with the exception that the water from well #4 in Wausau, WI was substituted for the organic-free water. Tables IV-1 and IV-2 show

Table IV-1 Summary of Isotherm Data for Raw Water and Spiked Raw Water from Well #4 in Wausau, WI Using W-VG Carbon (200 x 400 mesh).

Sample Date & Experimenter	Equilibration Time, pH, Temp	Comments	Immediate Blanks & Concentration Range (ug/L)								
			DCE	TCE	PCE	Tol	E.B.	m-Xy	op-Xy	TOX	TOC
10/25/83 Luft(1984)	3.0 days, pH=6.0 $11^{0}C \pm 1^{0}C$	TCE spiked (Buffered)	425	682 3-560	104	104	NA	NA	NA	NA	NA
2/20/84 Luft(1984)	6.0 days, pH=6.2 $10^{0}C \pm 1^{0}C$	DCE spiked (Buffered)	1240 (183-1310)	120	80	100	13	21	30	NA	NA
2/20/84 Luft(1984)	6.0 days, pH=6.2 $10^{0}C \pm 1^{0}C$	TCE spiked (Buffered)	140	1020 (5-668)	80	100	13	21	30	NA	NA
2/20/84 Luft(1984)	6.0 days, pH=6.2 $10^{0}C \pm 1^{0}C$	PCE spiked (Buffered)	140	120	1790 (45-1440)	100	13	21	30	NA	NA
10/12/84 Luft(1984)	7.0 day, pH=6.8 $12^{0}C \pm 1^{0}C$	TCE spiked (No Buffer)	74 (6-50)	517 (3-175)	58.5 (1-8)	37.9 (ND-1)	5.1 (ND-3)	6.7 ND	10.2 ND	155	8550

DCE = Cis-1,2 Dichloroethene
TCE = Trichloroethene
PCE = Tetrachloroethene
Tol = Toluene
E.B. = Ethylbenzene
m-Xy = m-xylene
o,p-Xy = o,p-xylene

NA = not available
ND = not detectable

Table IV-2 Summary of Isotherm Data for Raw Water and Spiked Raw Water from Well #4 in Wausau, WI Using F-400 Carbon (200x400 mesh).

Sample Date & Experimenter	Equilibration Time, pH, Temp	Comments	Immediate Blanks & Concentration Range (ug/L) DCE	TCE	PCE	Tol	E.B.	m-Xy	op-Xy	TOX	TOC
10/25/83 Luft(1984)	5.0 days, pH=6.0 $10^oC \pm 1^oC$	TCE spiked (Buffered)	425	604 (3-320)	104	104	NA	NA	NA	NA	NA
2/20/84 Luft(1984)	6.0 days, pH=6.2 $10^oC \pm 1^oC$	DCE spiked (Buffered)	1170 (143-1090)	120	80	100	13	21	30	NA	NA
2/20/84 Luft(1984)	6.0 days, pH=6.2 $10^oC \pm 1^oC$	TCE spiked (Buffered)	140	1001 (13-720)	80	100	13	21	30	NA	NA
2/20/84 Luft(1984)	4.0 days, pH=6.2 $10^oC \pm 1^oC$	TCE spiked (Buffered) Presaturated: 62.5% Purged Wausau Water	140	896 (9-56)	80	100	13	21	30	NA	NA
2/20/84 Luft(1984)	6.0 days, pH=6.5 $10^oC \pm 1^oC$	TCE spiked (Buffered) diluted with 30% Milli-Q Water	140	1030 (9-560)	80	100	13	21	30	NA	NA
2/20/84 Luft(1984)	7.0 days, pH=6.3 $10^oC \pm 1^oC$	PCE spiked (Buffered)	140	120	1731 (11-890)	100	13	21	30	NA	NA
10/12/84 Kato(1985)	7.0 days, pH=6.8 $12^oC \pm 1^oC$	TCE spiked (No Buffer)	74.0^* (8-42)	520.0 (8-168)	58.5^* (1.20)	37.9^* (ND-2)	5.1^* (ND-1)	6.7^* (ND-1)	10.2^* (ND-2)	155	8550

(Continued)

Table IV-2 (Continued) Summary of Isotherm Data for Raw Water and Spiked Raw Water from Well #4 in Wausau, WI Using F-400 Carbon (200 x 400 mesh) continued.

Sample Date & Experimenter	Equilibration Time, pH, Temp	Comments	Initial Concentrations & Concentration Range (ug/L) DCE	TCE	PCE	Tol	E.B.	m-Xy	op-Xy	TOX	TOC
12/6/84 Hand(1985)	6 days, pH=6.3 12°C ± 1°C	(No Buffer) TOX	79.8	54.4	41.8	12.2	3.7	3.7	6.6	130 (6-35)	7720
4/8/85 Hand(1985)	7 days, pH=6.4 13.8°C ± 1°C	Raw Water (No Buffer)	70.7* (9-50)	34.1* (ND-16)	36.2* (ND-14)	18.3*	4.7*	5.1*	9.4*	116	8200
4/8/85 Hand(1985)	8 days, pH=6.3 13.8°C ± 1°C	(No Buffer) TOX	70.7*	34.1*	36.2*	18.3*	4.7*	5.1*	9.4*	118 (2-85)	8200
4/8/85 Hand(1985)	8 days, pH=6.3 13.8°C ± 1°C	(No Buffer) (diluted) TOX	70.7*	34.1*	36.2*	18.3*	4.7*	5.1*	9.4*	M (4-50)	8200
5/2/85 Hand(1985)	10 days, pH=6.3 13.8°C ± 1°C	(No Buffer) TOC	NA	NA	NA	NA	NA	NA	NA	135	8080 (710-4550)
3/30/86 Speth(1986)	10 days, pH=6.3 13.8°C ± 1°C	(No Buffer) TOC	NA	NA	NA	NA	NA	NA	NA	NA	8680 (1160-7920)

DCE = Cis-1,2 Dichloroethene
TCE = Trichloroethene
PCE = Tetrachloroethene
Tol = Toluene
E.B. = Ethylbenzene
m-Xy = m-xylene
o,p-Xy = o,p-xylene

NA = not available
ND = not detectable
M = Calculated from individual mass balances
BD = Considered to be bad data
TOX = Total Organic Halogen
TOC = Total Organic Carbon
* = Shown to degradate over the equilibration time of isotherm

the summary of all the Wausau water isotherms performed by various researchers at Michigan Technological University on WV-G and F-400 carbon, respectively. The isotherm data sheets can be found in Appendix IV. In almost all of the cases, the compound of interest was spiked into the Wausau water to improve the analytical results. These isotherms were then compared to those conducted in organic-free water to determine whether there is any additional competition present in the Wausau water.

Figures IV-1 through IV-5 compare the results of the spiked isotherms conducted in Wausau water to those conducted in organic-free water for DCE, TCE, and PCE. Shown in Figures IV-1 and IV-2 are the comparisons for DCE on F-400 and WV-G carbon, respectively. In both cases, competition due to the background has caused a large reduction in capacity for DCE for the Wausau water as compared to that in organic-free water. The reduction in capacity is especially present at high liquid-phase concentrations which correspond to small carbon dosages. The strongly-adsorbing compounds saturate the small amount of carbon leaving few adsorption sites for the weaker adsorbing compounds such as DCE. It must be noted that the error in the capacity becomes very large at low carbon dosages because the equilibrium concentration is very close to the initial concentration.

Shown in Figures IV-3 and IV-4 are the comparisons for TCE on F-400 and WV-G carbons, respectively. For both carbons, a reduction in capacity is observed for the isotherms conducted in the presence of the Wausau water. This reduction in capacity is not as large as that observed for DCE because TCE is a more strongly-adsorbing compound.

Figure IV-5 displays the isotherm comparison for PCE on F-400 carbon. Only a slight reduction in capacity is observed for PCE

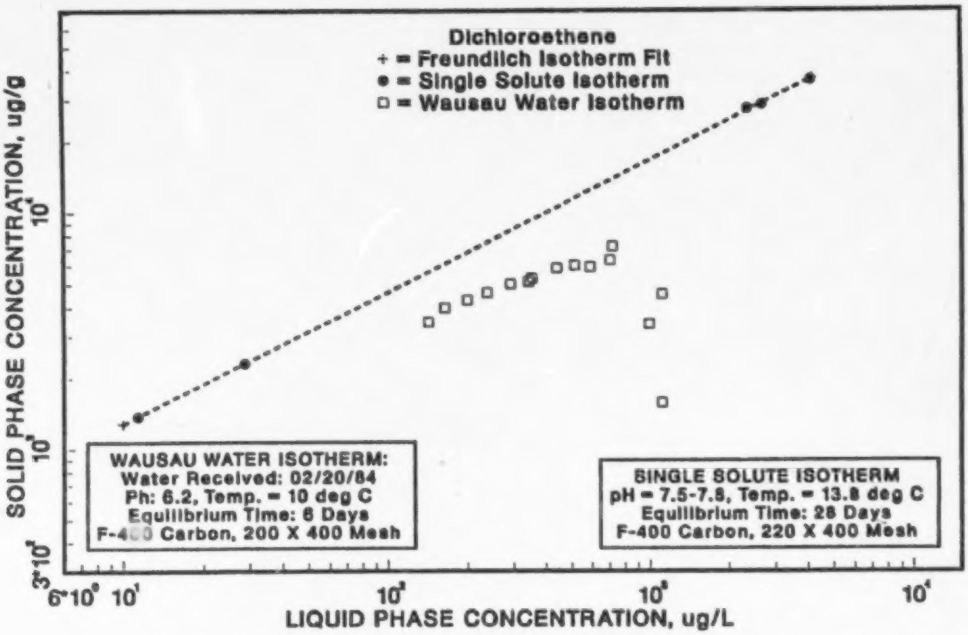

Figure IV-1. Comparison of Single Solute Isotherm Data to Isotherm Data Conducted in Wausau Water for cis 1,2-Dichloroethene on F-400 Carbon.

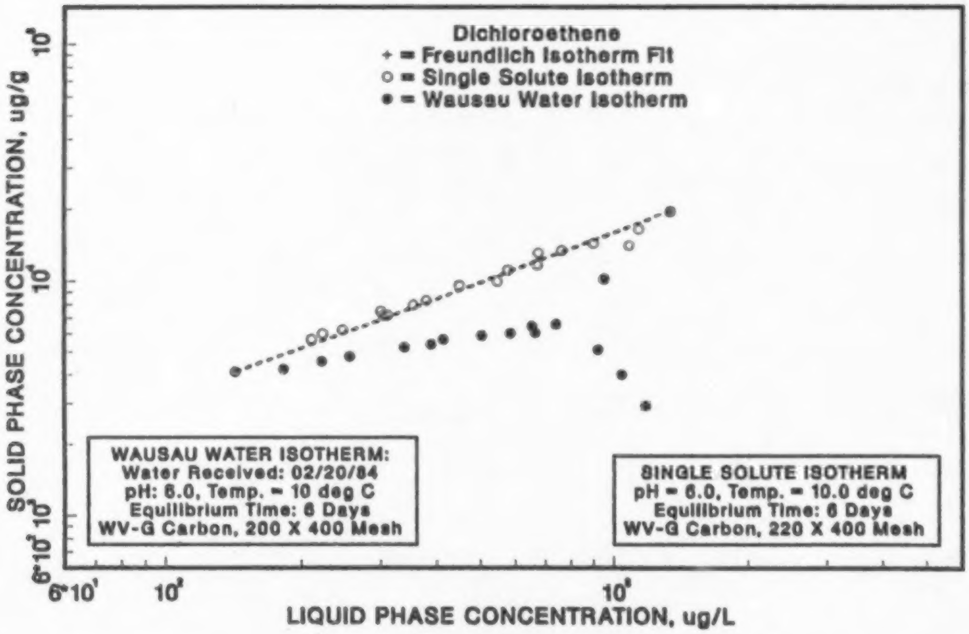

Figure IV-2. Comparison of Single Solute Isotherm Data to Isotherm Data Conducted in Wausau Water for cis 1,2-Dichloroethene on WV-G Carbon.

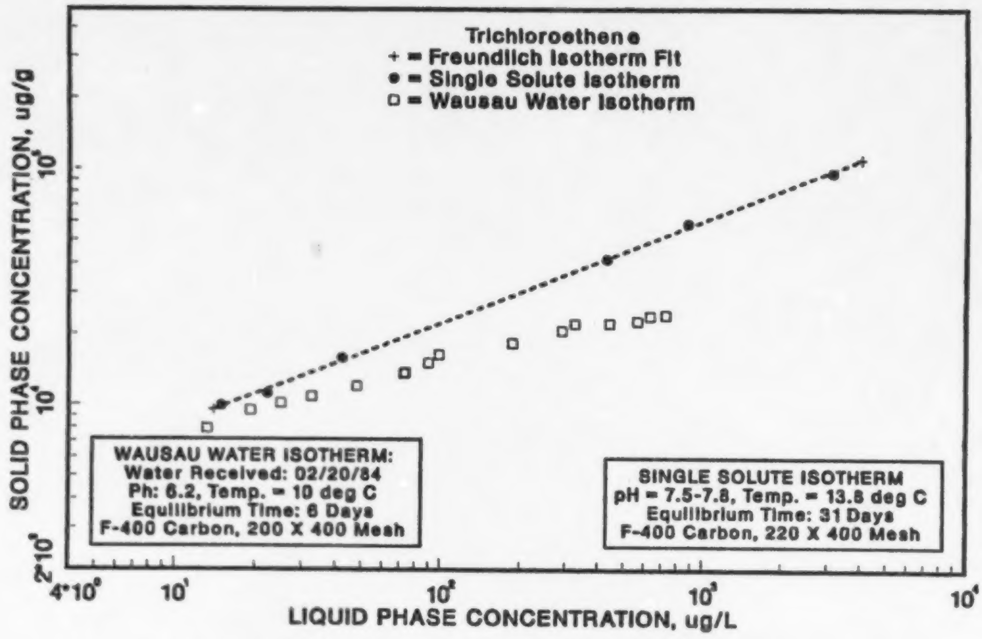

Figure IV-3. Comparison of Single Solute Isotherm Data to Isotherm Data Conducted in Wausau Water for Trichloroethene on F-400 Carbon.

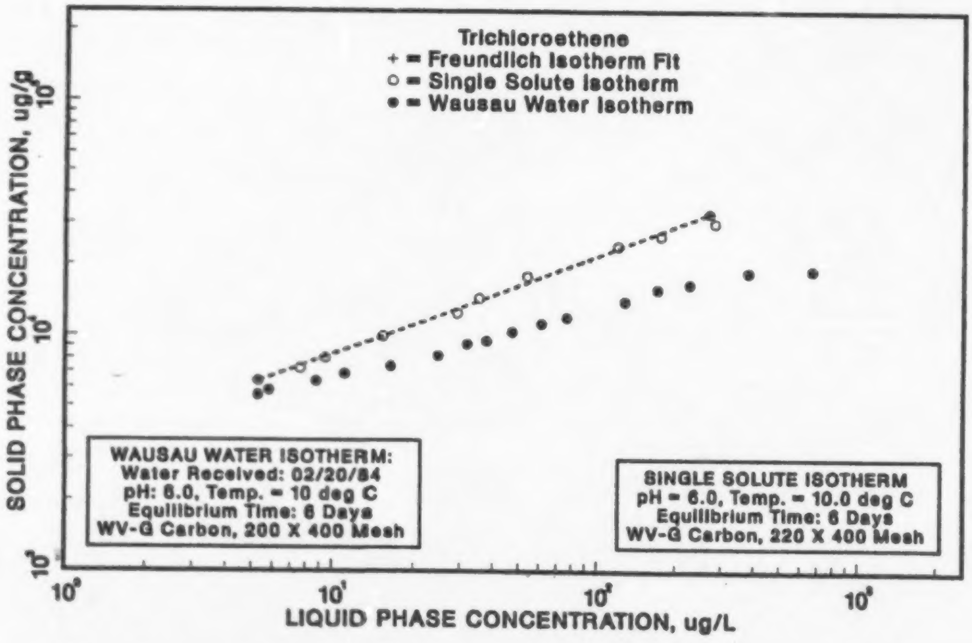

Figure IV-4. Comparison of Single Solute Isotherm Data to Isotherm Data Conducted in Wausau Water for Trichloroethene on WV-G Carbon.

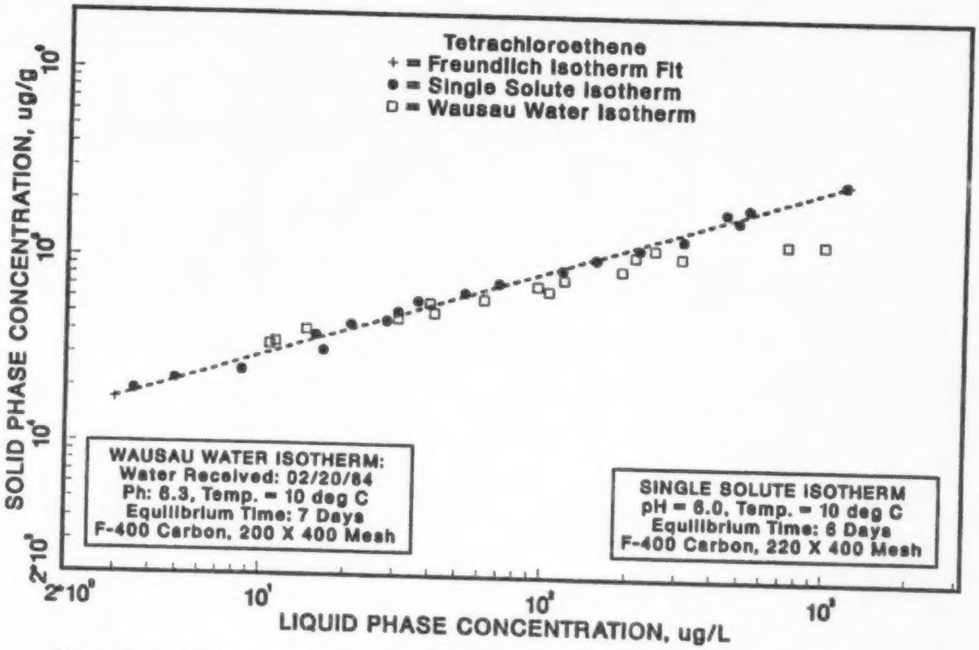

Figure IV-5. Comparison of Single Solute Isotherm Data to Isotherm Data Conducted in Wausau Water for Tetrachloroethene on F-400 Carbon.

because it is much more strongly adsorbed than DCE or TCE.

B. PREDICTION OF COMPETITIVE INTERACTIONS IN THE WAUSAU WATER USING IDEAL ADSORBED SOLUTION THEORY

The results that were presented in Figures IV-1 through IV-5 show that significant competition exists between the individual VOCs and the remaining organic background present in the Wausau water. If this competition is only caused by the VOCs present in the Wausau water, then it may be possible to predict the competition using ideal adsorbed solution theory (IAST). Appendix VIII contains a listing of the program. To use IAST, the single solute isotherm parameters and initial concentrations of all the compounds must be known. The VOCs present in the Wausau water, other than DCE, TCE and PCE are toluene, ethyl benzene, m-xylene, and o,p-xylene.

The isotherm parameters shown in Table II-3 were used for modeling except for the 10-25-83 and the 2-20-84 data where the single solute PCE isotherm performed by Luft was used. Luft also completed the spiked Wausau water isotherms on these dates and it is expected that there are analytical similarities between the single solute and Wausau water isotherms. Figures IV-6 and IV-7 show the IAST predictions for the 10-25-83 Wausau water TCE isotherms on WV-G and F-400 carbon, respectively. Figures IV-8 through IV-12 display the IAST predictions for the 2-20-84 Wausau water DCE, TCE, and PCE isotherms on both carbons. Figures IV-13 and IV-14 display the IAST predictions for the 10-12-84 Wausau water TCE isotherms on WV-G and F-400 carbon, respectively.

For the WV-G predictions, the Freundlich parameters for toluene, ethyl benzene, o,p-xylene, and m-xylene were found from the Polanyi

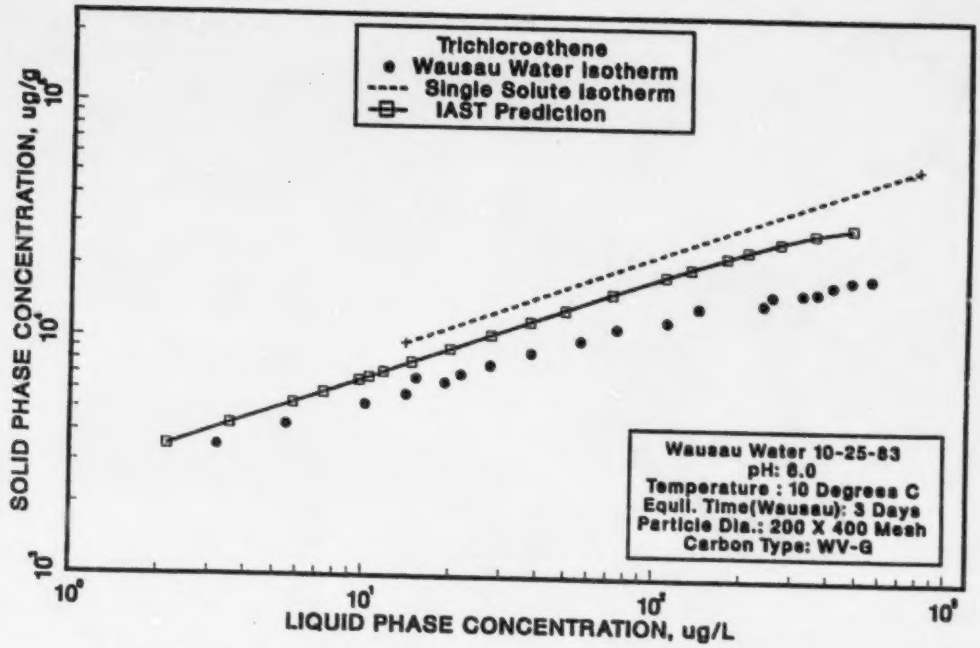

Figure IV-6. Trichloroethene F-400 Carbon Isotherm Data Conducted in Wausau Water on 10-25-83 with IAST Model Prediction and Single Solute Isotherm.

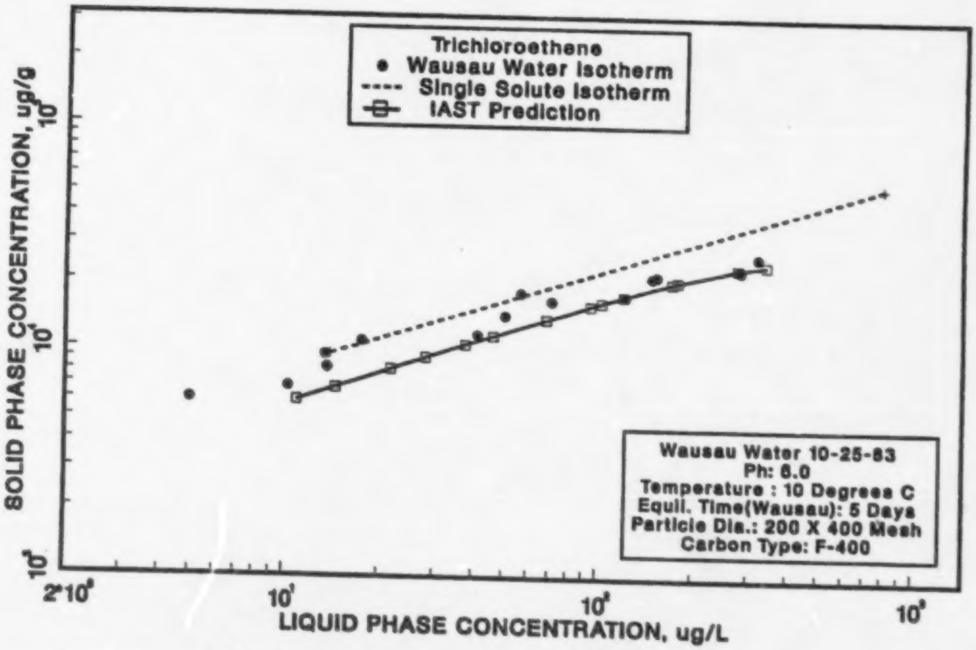

Figure IV-7. Trichlorcethene WV-C Carbon Isotherm Data Conducted in Wausau Water on 10-25-83 with IAST Model Prediction and Single Solute Isotherm.

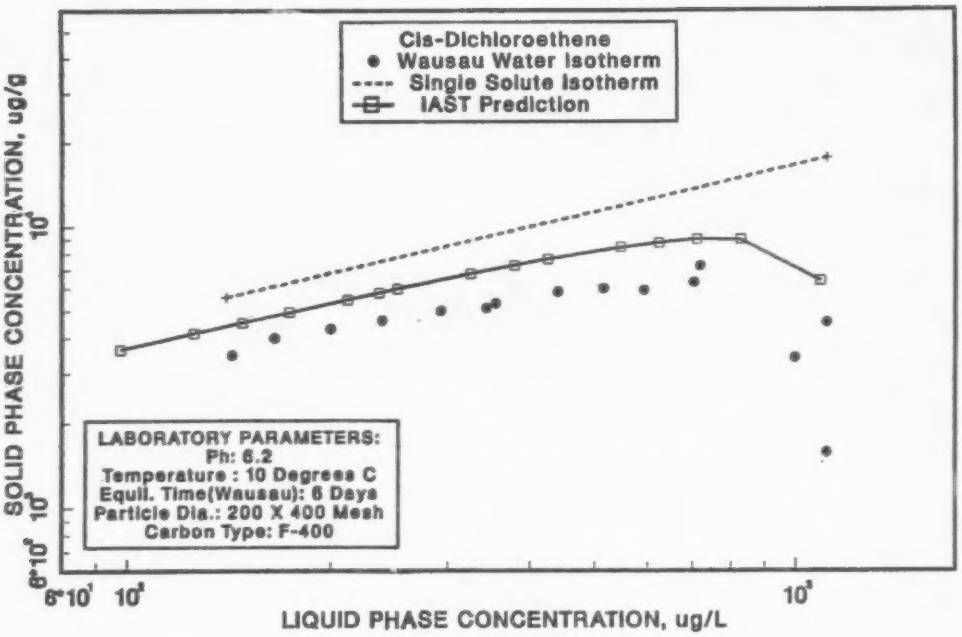

Figure IV-8. Cis 1,2-Dichloroethene F-400 Carbon Isotherm Data Conducted in Wausau Water on 2-20-84 with IAST Model Prediction and Single Solute Isotherm.

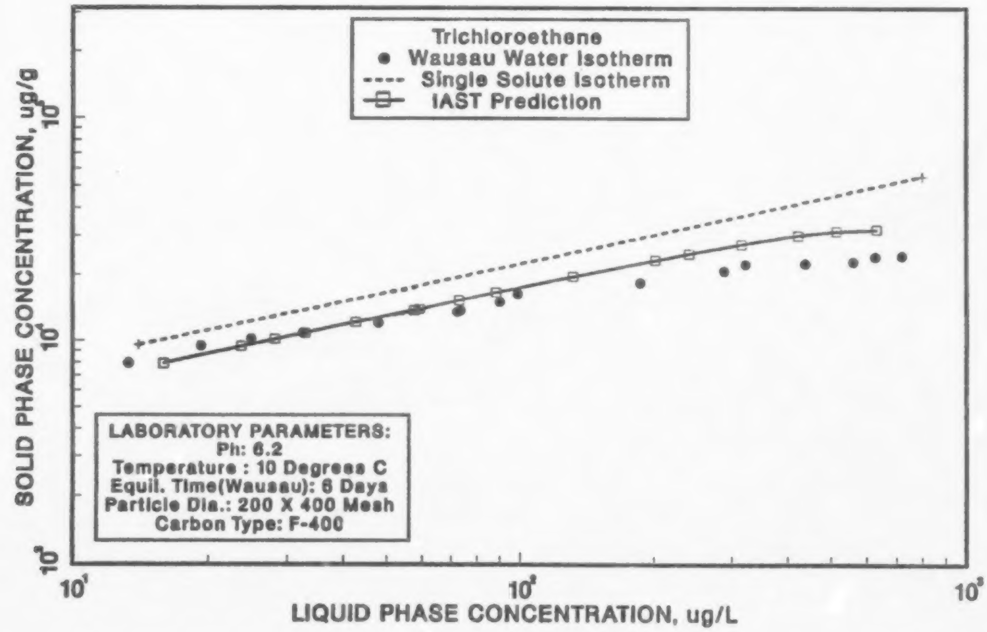

Figure IV-9. Trichloroethene F-400 Carbon Isotherm Data Conducted in Wausau Water on 2-20-84 with IAST Model Prediction and Single Solute Isotherm.

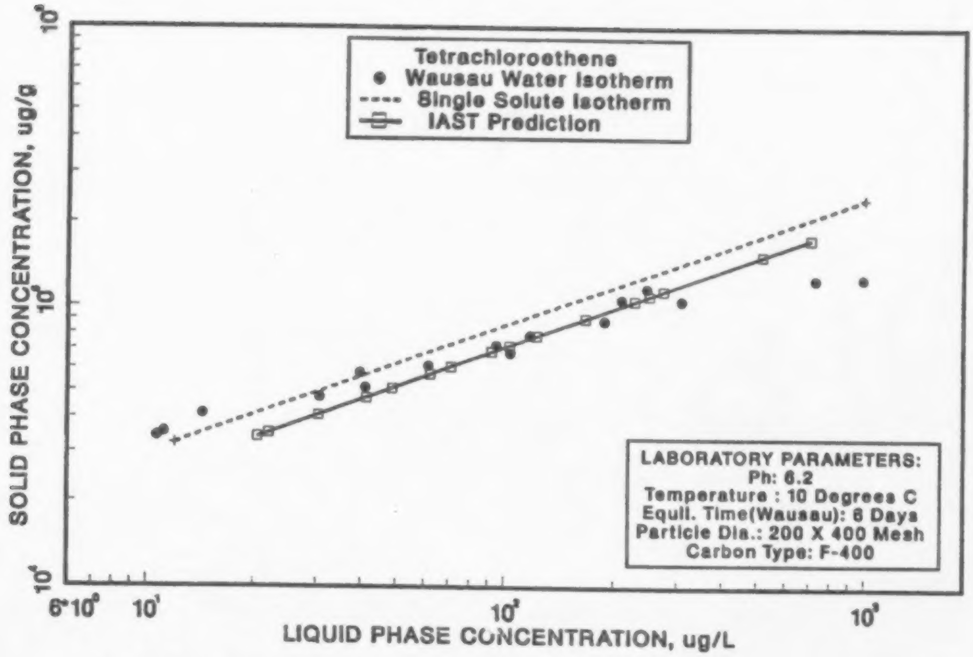

Figure IV-10. Tetrachloroethene F-400 Carbon Isotherm Data Conducted in Wausau Water on 2-20-84 with IAST Model Prediction and Single Solute Isotherm.

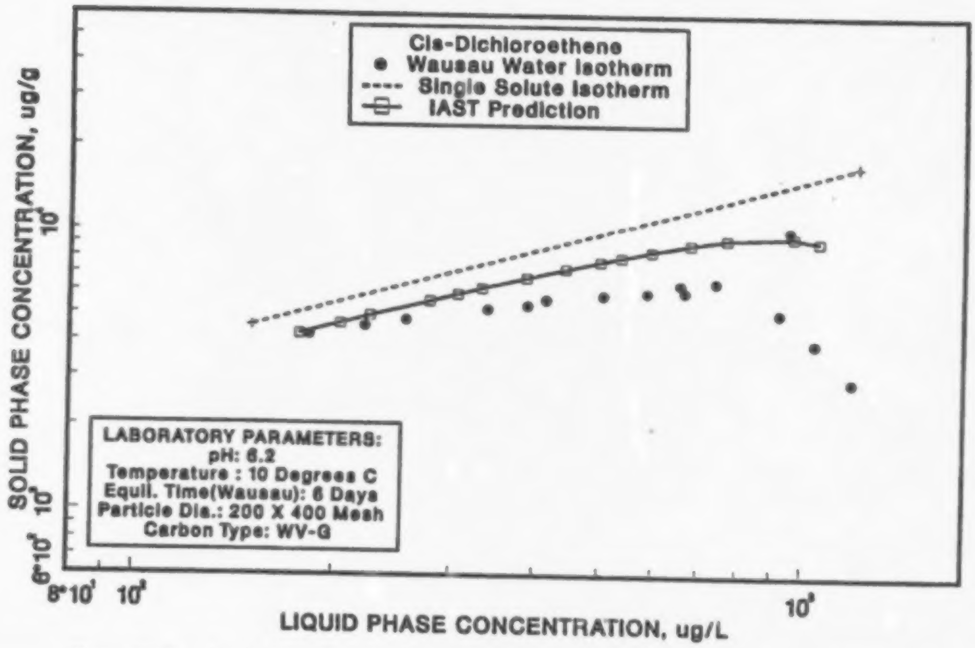

Figure IV-11. Cis 1,2-Dichloroethene WV-G Carbon Isotherm Data Conducted in Wausau Water on 2-20-84 with IAST Model Prediction and Single Solute Isotherm.

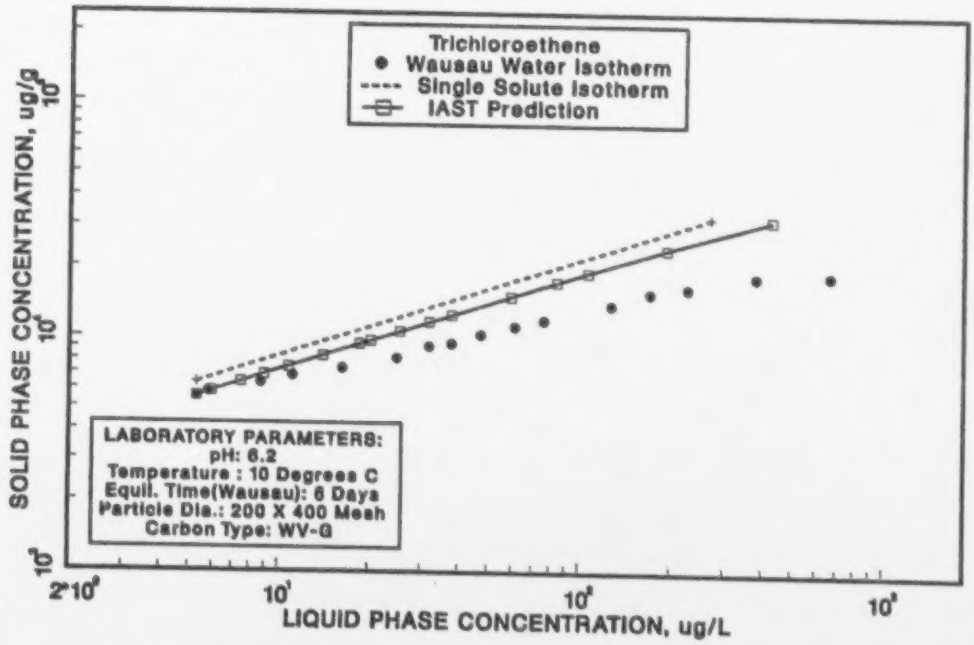

Figure IV-12. Trichloroethene WV-G Carbon Isotherm Data Conducted in Wausau Water on 2-20-84 with IAST Model Prediction and Single Solute Isotherm.

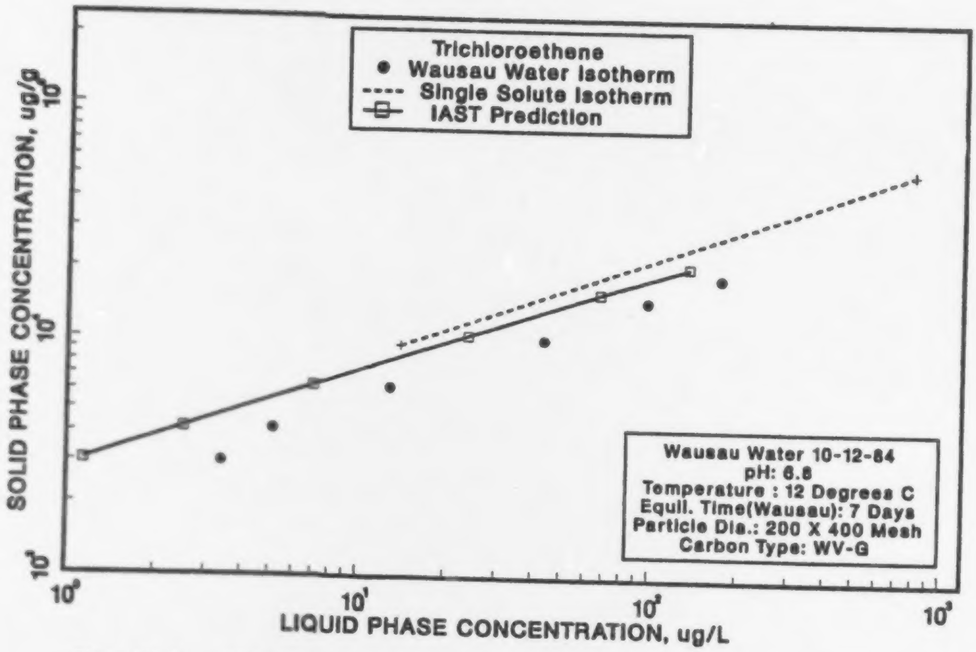

Figure IV-13. Trichloroethene WV-G Carbon Isotherm Data Conducted in Wausau Water on 10-12-84 with IAST Model Prediction and Single Solute Isotherm.

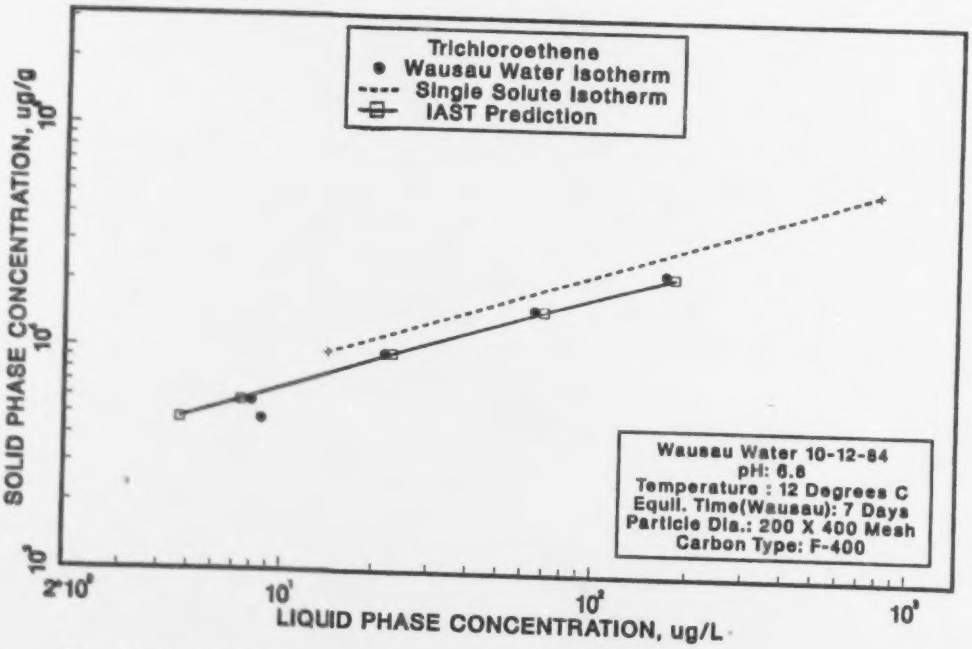

Figure IV-14. Trichloroethene F-400 Carbon Isotherm Data Conducted in Wausau Water on 10-12-84 with IAST Model Prediction and Single Solute Isotherm.

potential theory as discussed in section III. Because the slope of the characteristic curve for the WV-G carbon is very dependent on the PCE isotherm as shown in Figure III-6, the predictions for toluene, ethyl benzene, o,p-xylene, m-xylene seem to be in error because the solubility predicted from UNIFAC for PCE may be higher than the actual value as shown in Table III-1. Therefore, the predictions for the Freundlich parameters of the other compounds could give results that indicate the compounds are weakly adsorbing. This can explain why the predictions for WV-G carbon Wausau water isotherms are much higher than the experimental data. The F-400 predictions are closer to the experimental data, but in most cases, the predicted capacity was slightly higher then the data which may indicate the background capacity has been slightly underestimated and adsorbing organic compounds other than those identified in the Wausau water are present.

It is interesting to note that for the 10-25-83 isotherms the compounds used in the IAST calculation excluding TCE are DCE, PCE, and toluene. Ethyl benzene, o,p-xylene, and m-xylene were not tested for on that date. From this, it would be expected that the prediction would lie much higher than the experimental data because not all of the background is being represented. However, this is not the case for the F-400 carbon isotherm as shown in Figure IV-7; the prediction lies slightly below the experimental data. This indicates that either the concentrations reported for DCE, PCE, and toluene are higher than the actual concentration, or the 10-25-86 F-400 carbon isotherm is in error.

Although there are some differences between the IAST predictions and the data, the predictions still represent fairly good estimates of the adsorbing capacity of the measured compounds in the presence of the background. In addition, these results indicate that the measured VOCs do represent most of the competitive adsorbing strength present in the Wausau water.

On 4-6-85, a Wausau water isotherm which was not spiked was completed on F-400 carbon. The Freundlich parameters which were used in the IAST calculation are listed in Table II-3. Figure IV-15 shows the Wausau water isotherm and the IAST predictions. In this case, IAST can be seen to predict the DCE isotherm but not the TCE and PCE isotherms. The isotherms for TCE and PCE are well below where they are expected because it appears that they were affected more by the background than DCE as seen by their offset from the single solute isotherms. Since TCE and PCE are more strongly adsorbed than DCE, they should be affected less by the background. The reason for the large error for TCE and PCE is because the VOCs underwent degradation over the equilibration time of the isotherm. This can be seen in Table IV-3.

Since the initial concentrations change over time, it is unclear what initial concentration values to use to calculate the mass adsorbed onto the carbon. Figure IV-15 was calculated using the equilibrated blanks. Using the immediate blanks, shown in Figure IV-16, DCE would come out on top of its single solute line, TCE would come out where it would be expected, and PCE would show a favorable change. Because of the DCE lying above the single solute line, it can be concluded that using the immediate concentrations is not correct either.

Dobrzelewski (1985) performed a study where the Wausau water was passed through a .22 micron filter. The results showed that this did not affect the degradation which suggests that the degradation is not

Table IV-3. Comparison of Immediately Extracted Blanks and Equilibrated Blanks for the 4/19/85 Wausau Water Isotherm.

Compound	Blank Analyzed Immediately After the Sample was Taken (μg/L)	Blank Analyzed After the Equilibration Time of Seven Days (μg/L)
Cis 1,2-Dichloroethene	70.7	53.6
Trichloroethene	34.1	22.8
Tetrachloroethene	36.2	24.3
111-Trichloroethene	0.7	0.5
Benzene	X	X
Toluene	18.3	0.2
Ethylbenzene	4.7	0.2
m-Xylene	5.1	2.2
o,p-Xylene	9.4	5.4
Vinyl Chloride	20.6	4.9

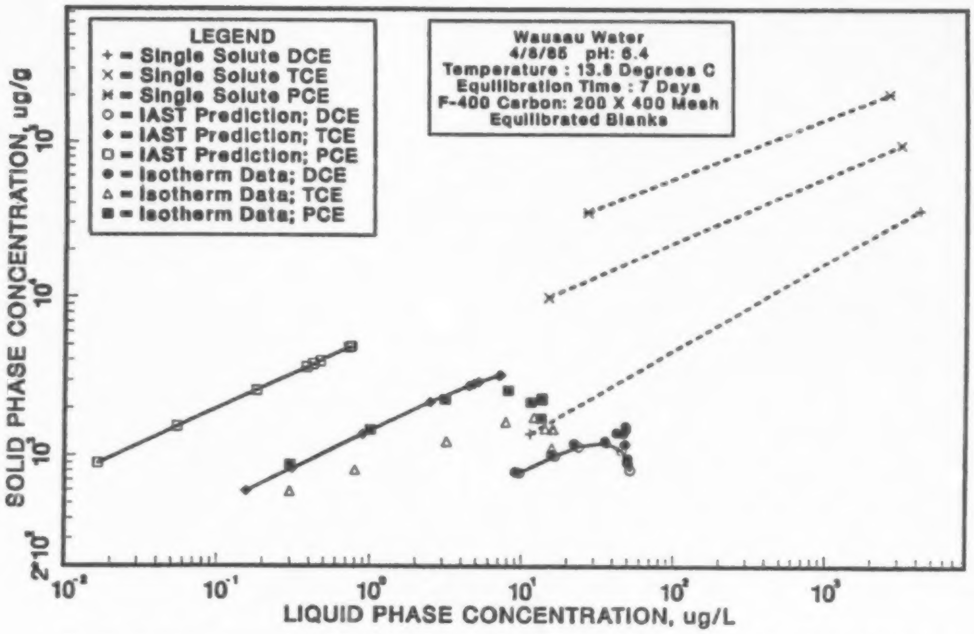

Figure IV-15. Multicomponent Isotherm Data Conducted in Wausau Water on F-400 Carbon Using Equilibrated Blanks with IAST Prediction and Single Solute Isotherm.

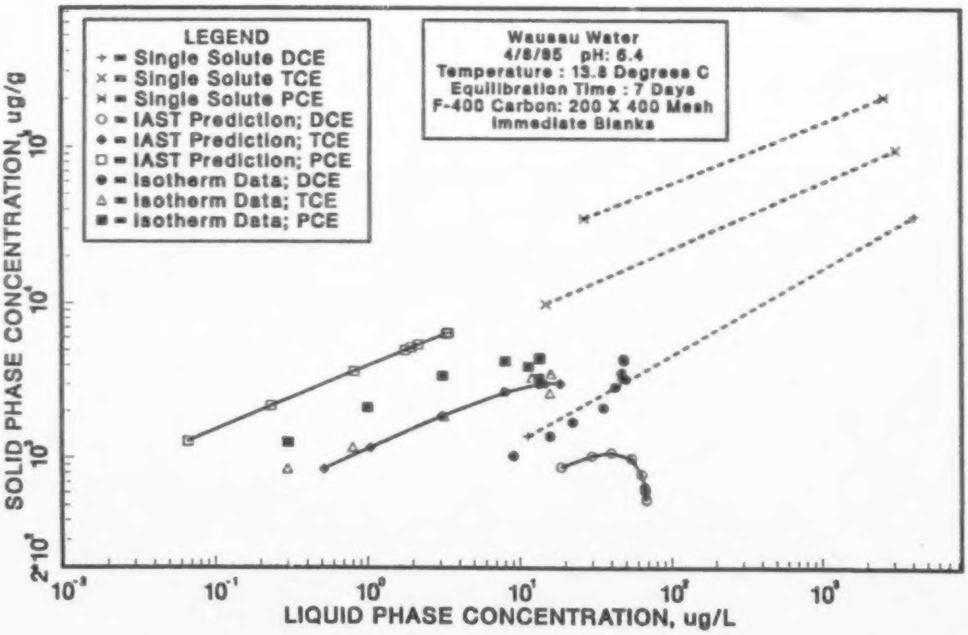

Figure IV-16. Multicomponent Isotherm Data Conducted in Wausau Water on F-400 Carbon Using Immediate Blanks with IAST Prediction and Single Solute Isotherm.

due to biodegradation, or that the organisms responsible are able to pass through a 0.22 micron filter. To decide the matter, mercuric chloride could be added to the water to destroy the organisms. However, mercuric chloride may affect isotherms by affecting the TOC.

Another possible problem with the 4-9-85 Wausau water isotherm is that the concentration of the single solute isotherm that is needed to assume equal spreading pressure for each component as reqnired by IAST is well below that of the single solute isotherm for every compound except DCE. This is not considered the major problem however. The equal spreading pressure concentration of the spiked isotherms were within the single solute concentration range for only TCE and PCE. For DCE it was above the range and for the rest it was below. One way to test to see if this causes a problem is to run single solute isotherms over a wider concentration range and see if the isotherms starts to show curvature. A way of seeing this is to take notice of the correlation curve shown in Figure III-5. The concentration ranges of the isotherms are extended because of the other components which are plotted over different adsorption potential ranges. Therefore, since the correlation curve is very close to being a straight line over the range of isotherms tested, the curvature of single solute isotherms would not be expected. Luft (1984) and Crittenden _et al._ (1985) discuss spreading pressure considerations.

C. PREDICTION OF COMPETITIVE INTERACTIONS IN THE WAUSAU WATER USING HYPOTHETICAL COMPONENTS

As discussed above, IAST modeling requires that the concentrations of the adsorbing compounds in the water matrix be known. This approach can be expensive and time consuming. Therefore, the competitive adsorption strength of the Wausau water was quantified by hypothetical components which can represent any portion of the adsorbing background. The required parameters for the hypothetical components are their initial concentrations, and their Freundlich K's and 1/n's. The Freundlich parameters can be obtained by either fitting a multicomponent isotherm for a specific component, or by fitting a TOC isotherm. These two methods will be discussed below.

1. Determination of Hypothetical Component Parameters by Fitting a Tracer Isotherm

The hypothetical component parameters for this method are obtained by first conducting an isotherm in the Wausau water using a tracer compound such as DCE. The tracer isotherm data is then fit using a parameter search algorithm (see Appendix IX) that incorporates IAST. For the studies that will be following, only one hypothetical component will be used. This hypothetical component will include all the components other than DCE, TCE, and PCE. It will allow us to predict Wausau water isotherms of TCE and PCE with the hypothetical components found from the Wausau water DCE isotherm without counting TCE or PCE in the hypothetical component.

Figures IV-17 through IV-21 display the fits that were obtained for DCE, TCE, and PCE on F-400 and WV-G carbon. All the fits were good except for the PCE fit in Figure IV-21. The reason for the poor PCE fit is because the multi-component isotherm lies above the single solute line at low liquid-phase concentrations. Because of this, the fit was weighted according to liquid-phase concentration. As can be seen, the fit is more accurate at high liquid-phase concentrations.

To prove that hypothetical components represent the true background, they must be able to predict other known components in the

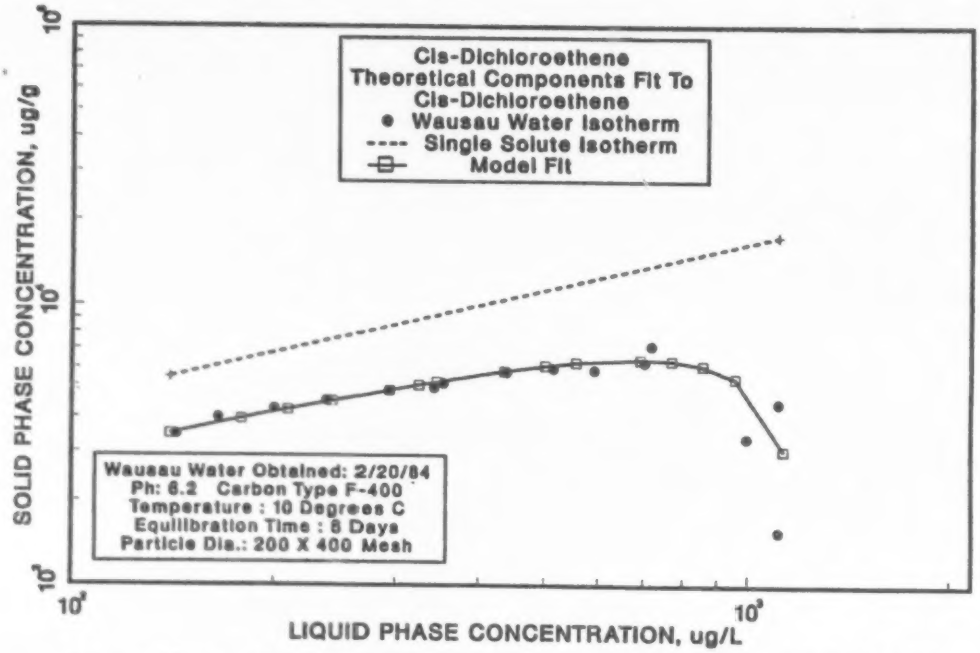

Figure IV-17. Cis 1,2-Dichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with Hypothetical Component Model Fit.

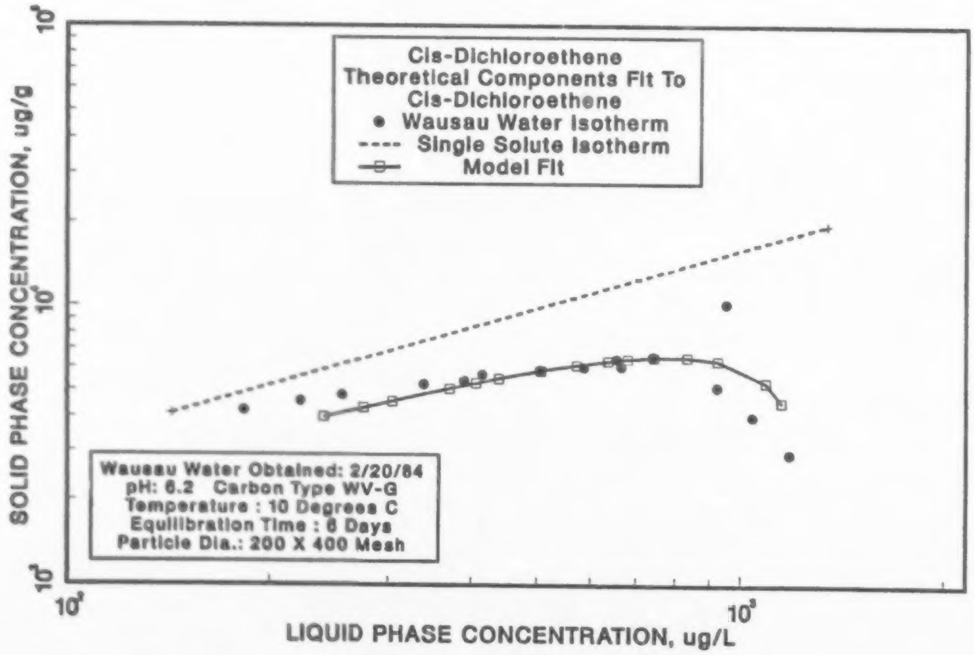

Figure IV-18. Cis 1,2-Dichloroethene Isotherm Data Conducted in Wausau Water on WV-G Carbon with Hypothetical Components Fit.

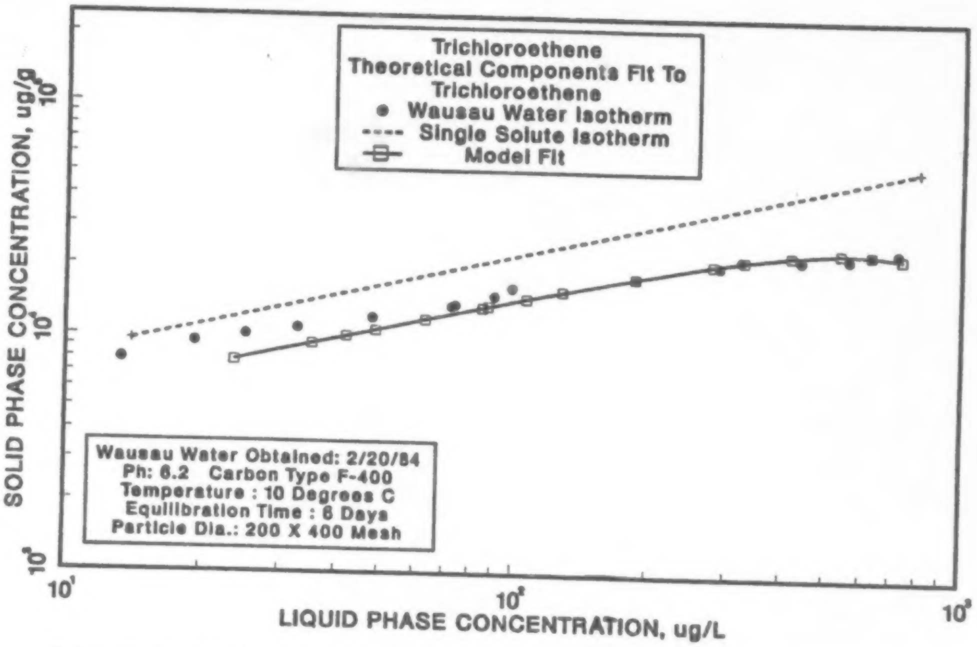

Figure IV-19. Trichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with Hypothetical Components Model Fit.

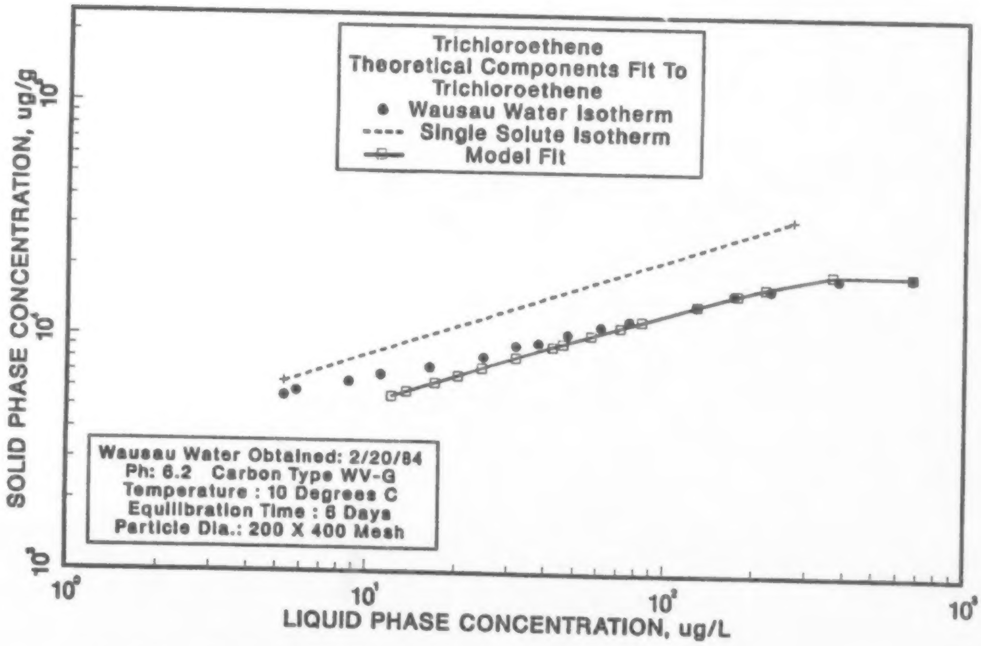

Figure IV-20. Trichloroethene Isotherm Data Conducted in Wausau Water on WV-G Carbon with Hypothetical Components Model Fit.

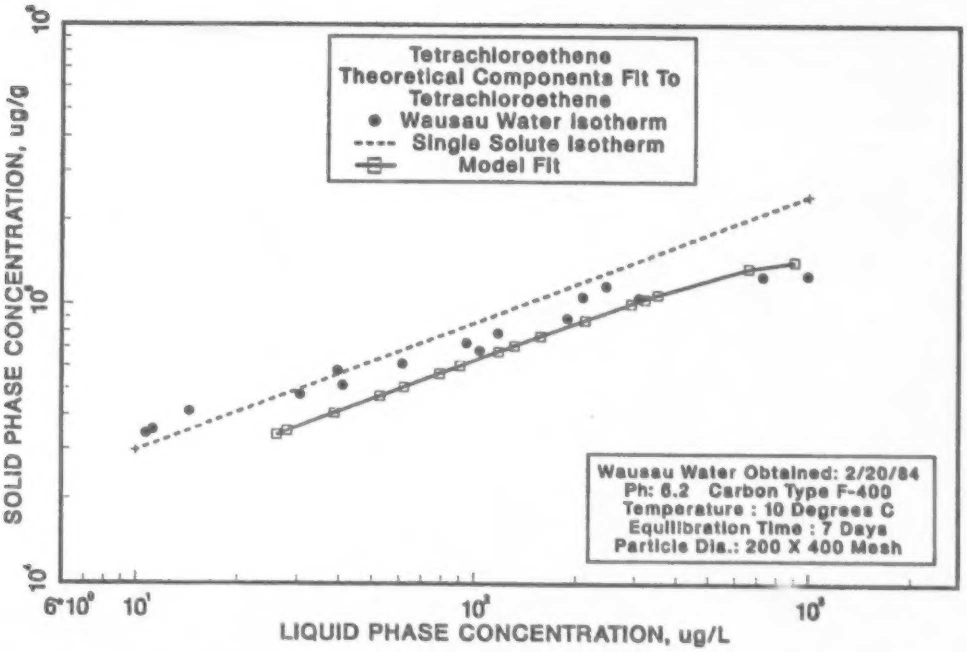

Figure IV-21. Tetrachloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with Hypothetical Components Model Fit.

Wausau water. Figures IV-22 and IV-23 represent the model predictions for TCE and PCE respectively, using the hypothetical components from the DCE tracer fit on F-400 carbon (Figure IV-17). Figures IV-24 and IV-25 are the model predictions for DCE and PCE using TCE as the tracer fit on F-400 carbon (Figure IV-19). Similarly, Figures IV-26 and IV-27 are the model predictions for DCE and TCE using PCE as the tracer component on F-400 carbon (Figure IV-21). Figure IV-28 is the model prediction for DCE on WV-G carbon using TCE as the tracer component (Figure IV-20), and Figure IV-29 is the model prediction for TCE on WV-G carbon using DCE as the tracer (Figure I-18). In all cases the predictions are quite accurate.

Table IV-4 presents the hypothetical component parameters other than DCE, TCE, and PCE obtained from the isotherm fits. Since they have been shown to predict Wausau water isotherms of other compounds, they should be of equal adsorbing strength for the specific carbons. The table shows clearly that there are many combinations of K, 1/n, and initial concentration that can give the same adsorbing strength.

In conclusion, hypothetical components found by fitting a tracer isotherm has been shown to be accurate in predicting the adsorption background and it may be advantageous to use it over the IAST technique because all of the adsorbing background can be taken into account.

2. Determination of Hypothetical Components by Fitting Total Organic Carbon Isotherms

Another method of determining hypothetical components is to fit a TOC isotherm. This is completed by varying the hypothetical components Freundlich parameters and initial concentrations until the liquid and solid-phase concentrations as found from IAST add up to form the TOC isotherm. Figure IV-30 shows total organic carbon isotherms for 5-2-85

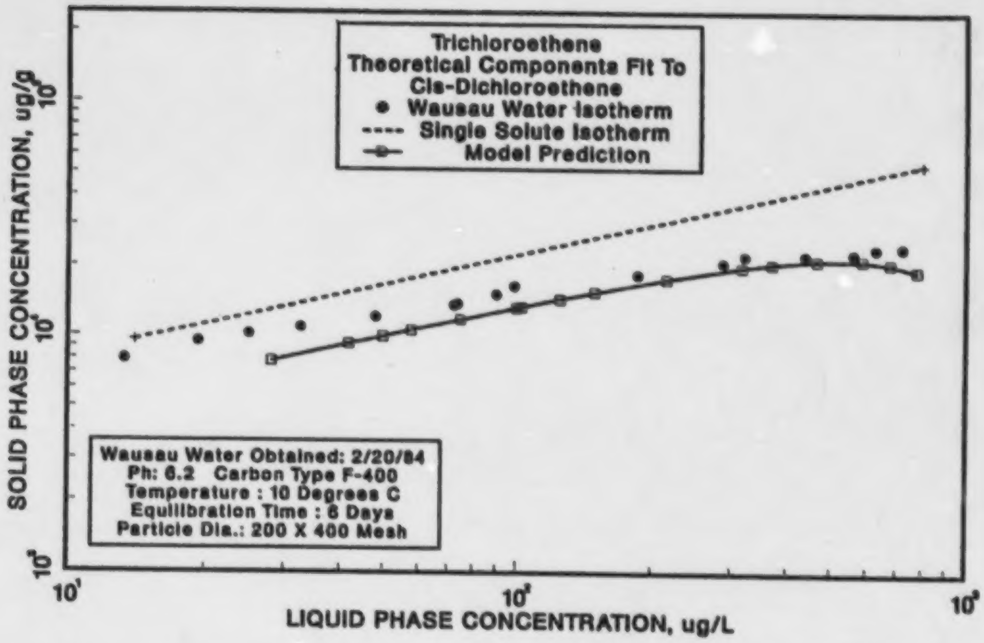

Figure IV-22. Trichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Component was Obtained from the Model Fit to the cis 1,2-Dichloroethene Isotherm Presented in Figure IV-18.

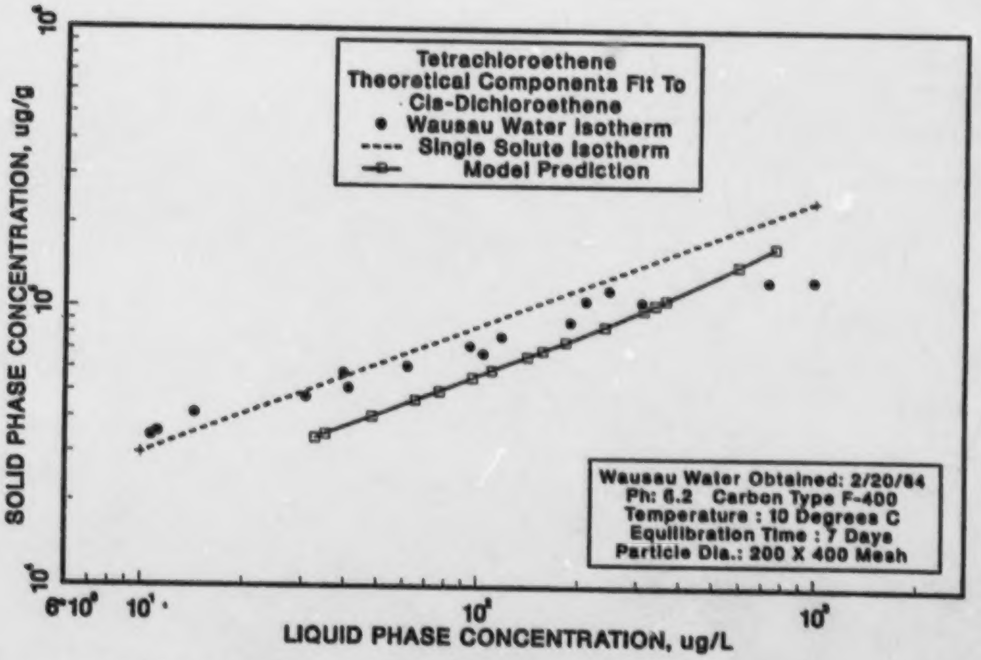

Figure IV-23. Tetrachloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Component was Obtained from the Model Fit to the cis 1,2 Dichloroethene Isotherm Presented in Figure IV-18.

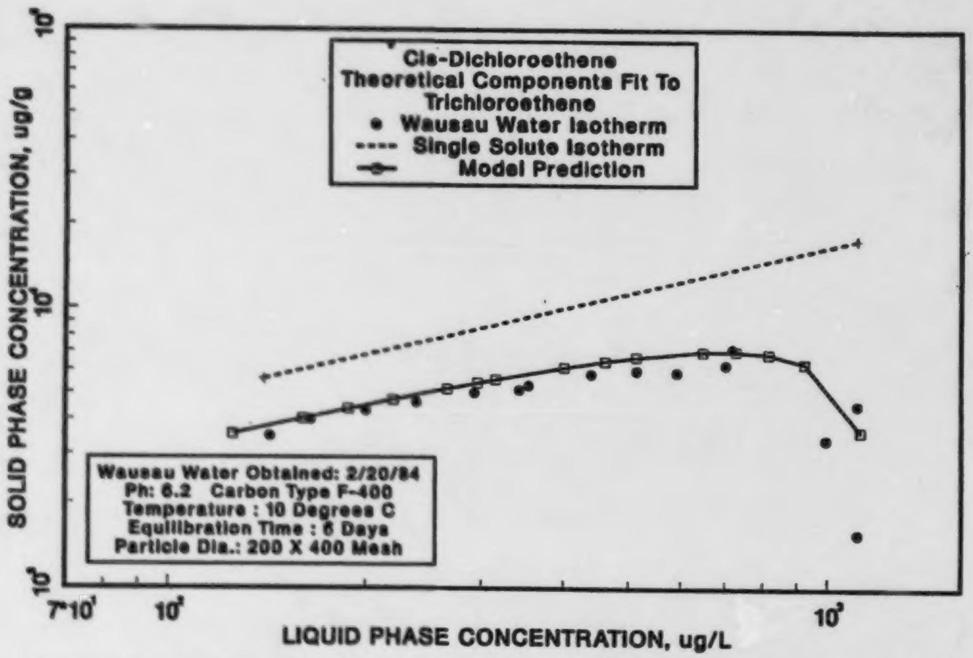

Figure IV-24. Cis 1,2-Dichloroethene Isotherm Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Component was Obtained from the Model Fit to the Trichloroethene Isotherm Presented in Figure IV-19.

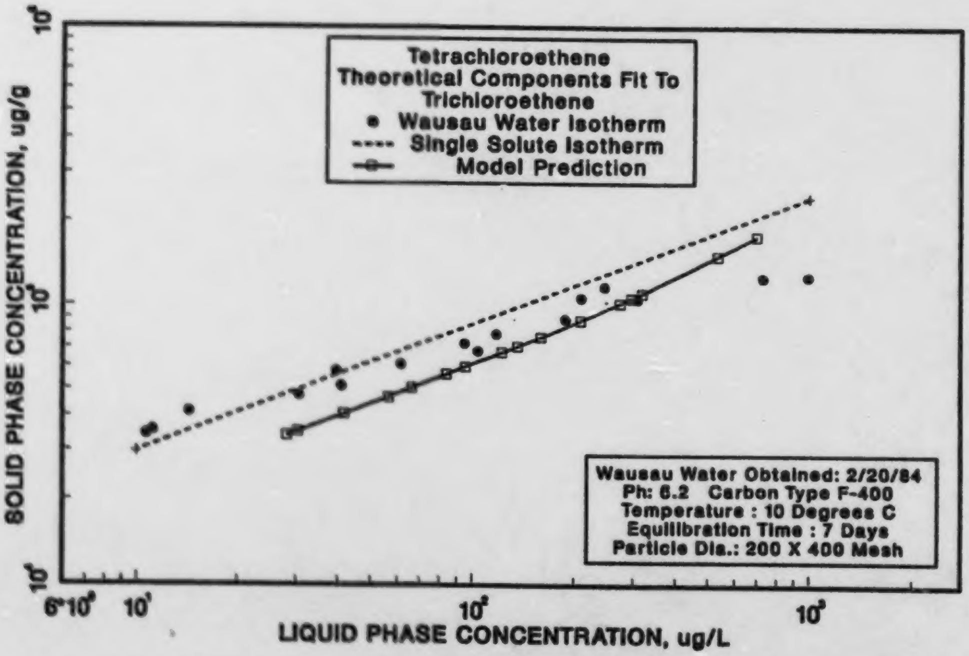

Figure IV-25. Tetrachloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypotaetical Component Model Prediction. The Hypothetical Components were Obtained from the Model Fit to the Trichloroethene Isotherm Presented in Figure IV-19.

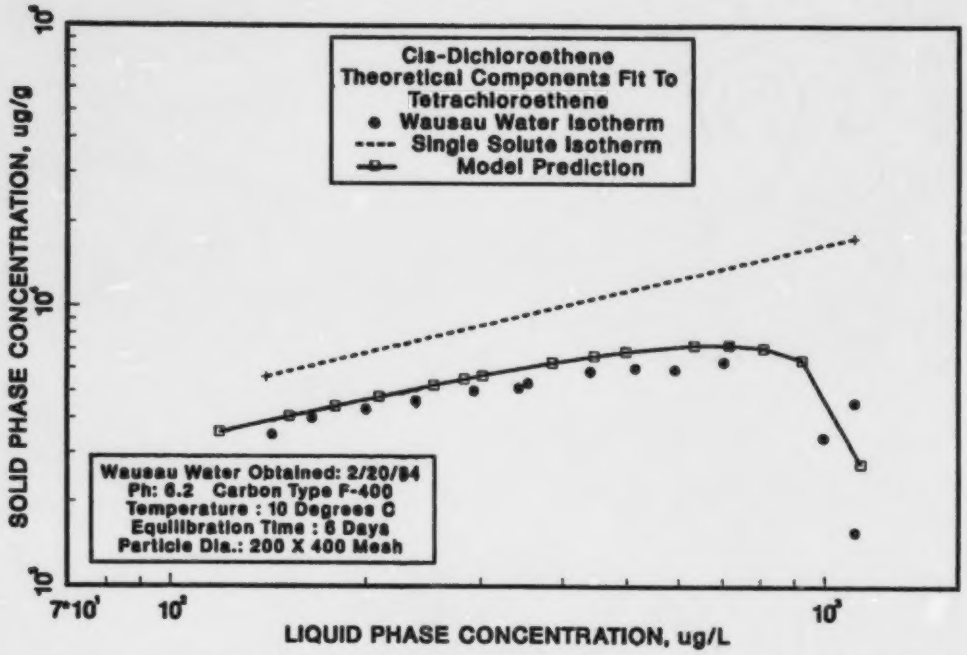

Figure IV-26. Cis 1,2-Dichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Components were Obtained from the Model Fit to the Tetrachloroethene Isotherm Presented in Figure IV-20.

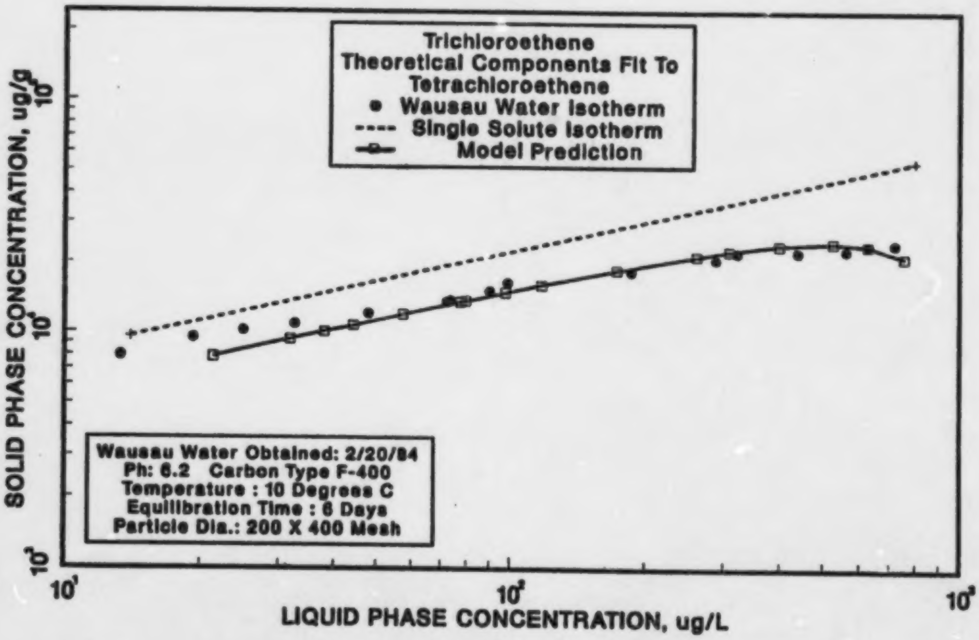

Figure IV-27. Trichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Component was Obtained from the Model Fit to the Tetrachloroethene Isotherm Data Presented in Figure IV-20.

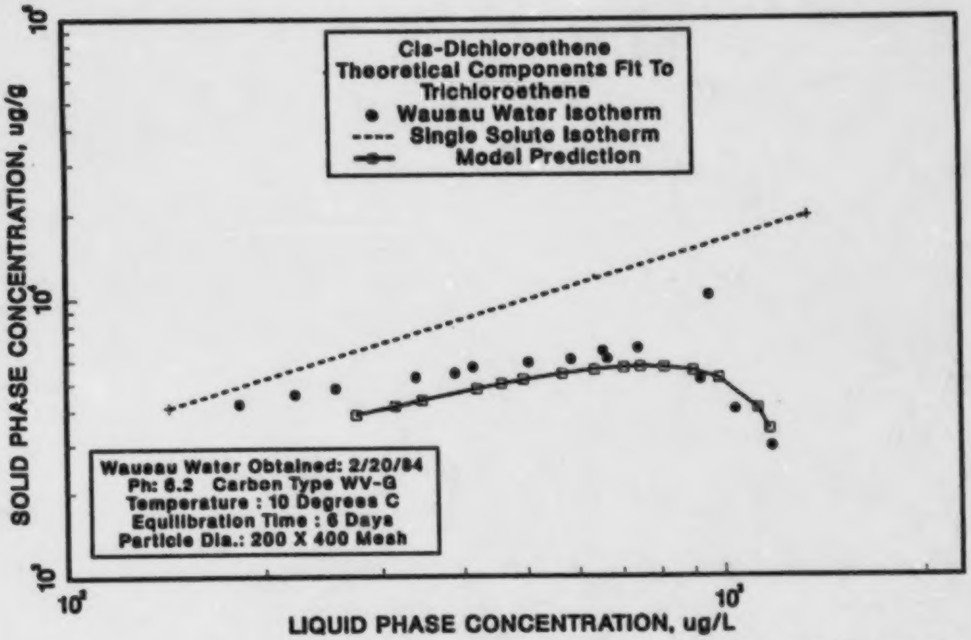

Figure IV-28. Cis 1,2-Dichloroethene Isotherm Data Conducted in Wausau Water on WV-G Carbon with the Hypothetical Component Model Prediction. The Hypothetical Component was Obtained from the Model Fit to the Trichloroethene Isotherm Data Presented in Figure IV-21.

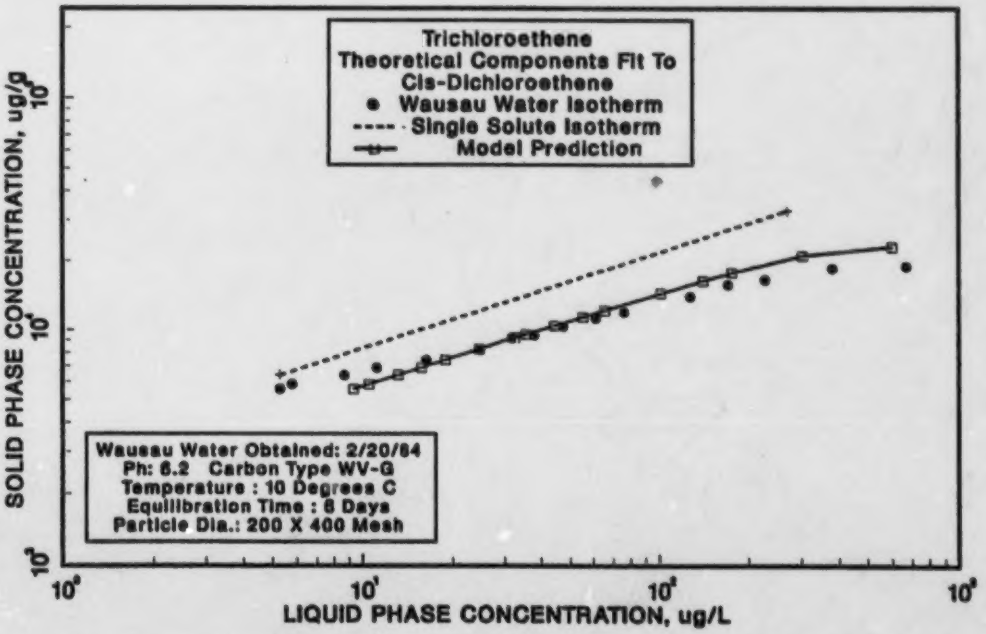

Figure IV-29. Trichloroethene Isotherm Data Conducted in Wausau Water on WV-G Carbon with the Hypothetical Component Model Prediction. The Hypothetical Component was Obtained from the Model Fit to the cis 1,2-Dichloroethene Isotherm Data Presented in Figure IV-2C.

Table IV-4. Summary of the Hypothetical Component Parameters found by Fitting Tracer Isotherms Completed in Wausau Water on 2-20-84.

		Hypothetical Component Parameters Representing All Compounds Except Cis-1,2-Dichloroethene, Trichloroethene, and Tetrachloroethene		
Tracer Component	Carbon Type	Freundlich K	Freundlich 1/n	Concentration (µmol/L)
Cis-1,2-Dichloroethene	F-400	406.9	0.2587	4.252
Trichloroethene	F-400	336.8	0.2433	2.958
Tetrachloroethene	F-400	1018.3	0.0845	0.683
Cis-1,2-Dichloroethene	WV-G	390.5	0.2220	2.451
Trichloroethene	WV-G	264.3	0.1877	2.858

Note: Units of K are $(\mu mol/gm)(L/\mu mol)^{(1/n)}$

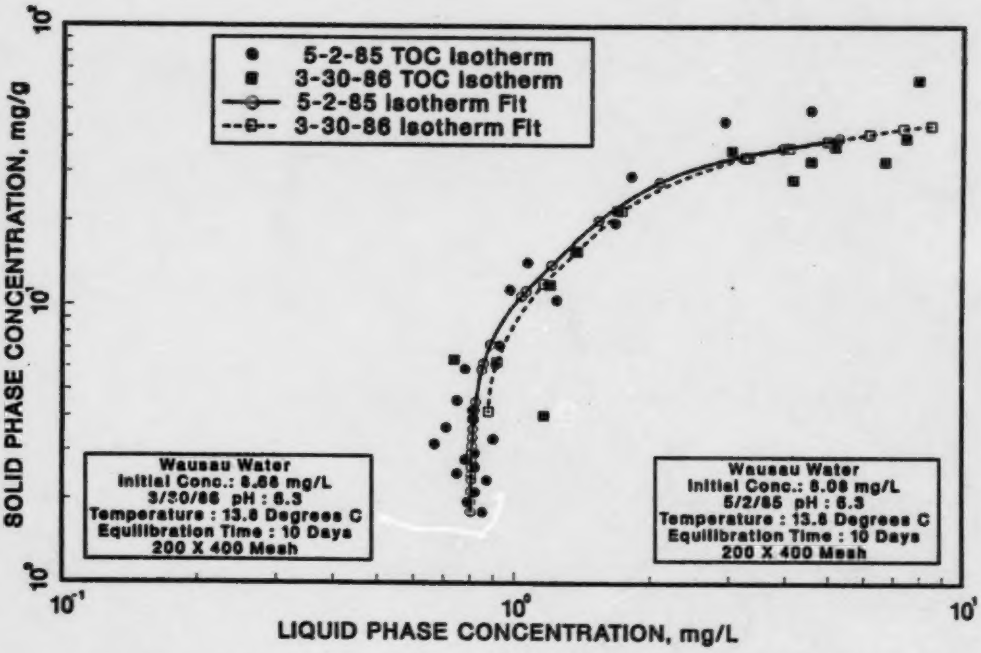

Figure IV-30. Total Organic Carbon Isotherm Completed in Wausau Water on F-400 Carbon with Hypothetical Component Fit.

and 3-30-86. The two isotherms seem to correspond indicating that the TOC adsorbing strength did not change between the dates of the isotherms. At high dosages, the solid-phase concentration drops to zero at a constant liquid-phase concentration. This indicates a non adsorbing fraction of TOC. From the figure, the nonadsorbing fraction seems to be 0.8 mg/L. The initial concentrations were 8.08 and 8.35 mg/L, therefore, approximately 10 percent of the TOC in the Wausau water is nonadsorbing.

By using a parameter search algorithm as written by Fettig et al. (1984), hypothetical components were found by fitting both TOC isotherms simultaneously. The model fit is also shown in Figure IV-30 The Freundlich parameters and initial concentrations of the hypothetical components can be seen in Table IV-5. Figures IV-31 and IV-32 show the prediction for DCE and TCE Wausau water isotherms for 2-20-84 using the hypothetical components found by fitting the TOC isotherm. As can be seen, the predictions are very poor. The reason for this is that when a TOC isotherm is fit, there are an extremely large number of combinations of hypothetical component parameters that will produce a satisfactorily fit; many more than by fitting a tracer isotherm.

One of the assumptions made was that the Wausau water matrix did not change between 2-20-84 and when the TOC isotherms were run. Because of the length of time between these isotherms, the assumption could be a very bad one, but because the predictions for the DCE and TCE isotherms were so poor that it can be concluded that no change in the Wausau water could result in an accurate prediction, and the prediction would be poor even if the isotherms were run on the same day.

Table IV-5. Summary of the Hypothetical Components Found by Fitting the 5-2-85 and 3-30-86 Total Organic Carbon Isotherms.

Hypothetical Component	Freundlich Parameters K $(\mu m/g)(L/\mu m)^{1/n}$	1/n	Initial Concentration C_o (mg of Carbon/L)
1	22.39	0.348	0.925
2	55.24	0.185	6.355
3	0.0	0.0	0.800

Note: Hypothetical component 3 represents the non-adsorbing fraction of TOC.

Note: The Freundlich K values are based on a molecular weight of 500 for TOC.

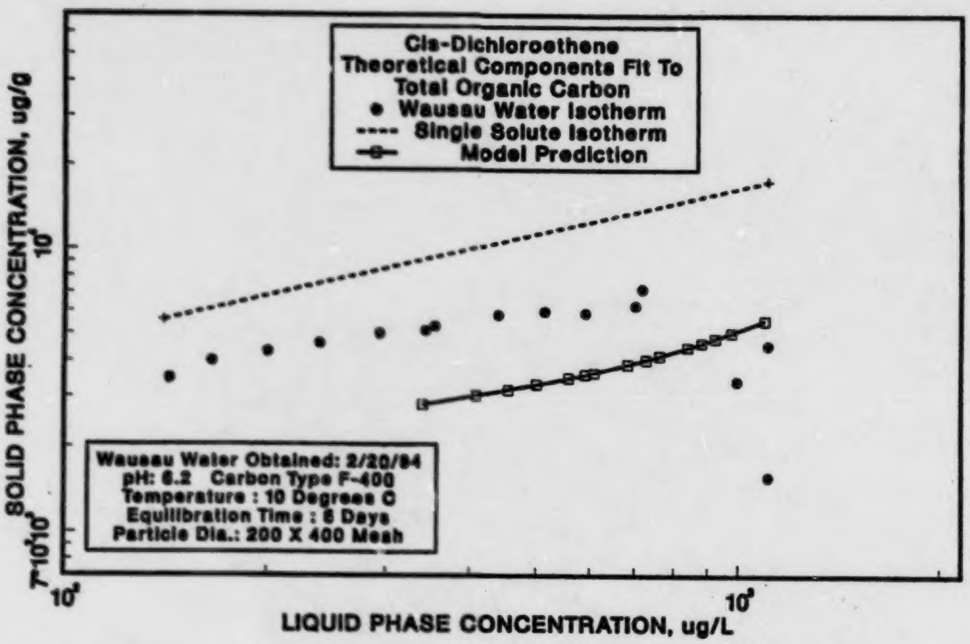

Figure IV-31. Cis 1,2-Dichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Components were Obtained from the Model Fit to the TOC Isotherms shown in Figure IV-30.

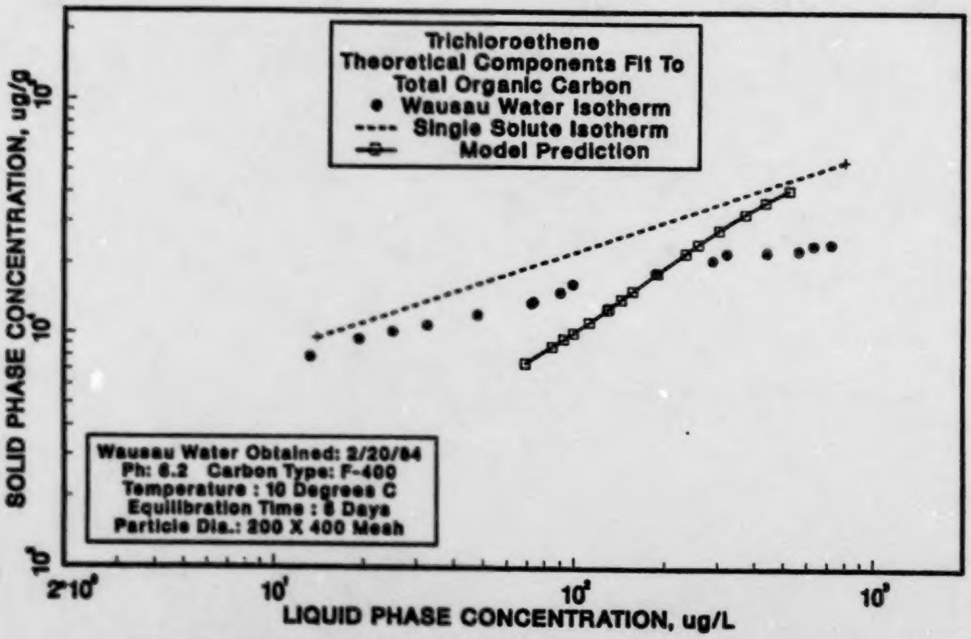

Figure IV-32. Trichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon with the Hypothetical Component Model Prediction. The Hypothetical Components were Obtained from the Model Fit to the TOC Isotherms shown in Figure IV-30.

Another possible problem is that the molecular weight of the TOC was assumed to be 500. This value was chosen because it was used in previous work at Michigan Technological University. No attempt was made to study the effects of changing the molecular weight of the TOC, or to complete experiments to determine the molecular weight.

To conclude, the hypothetical components found by fitting a TOC isotherm did a very inaccurate job in predicting single component Wausau water isotherms in this case.

3. Prediction of Competitive Interactions in the Wausau Water over Time Using Hypothetical Components

Figure IV-33 displays the concentration-history profiles of the known VOCs present in the Wausau groundwater obtained from well number 4. The concentrations of the VOCs in the groundwater have changed significantly with time. To determine the impact these concentration changes have on the competitive interactions, a comparison was made of isotherms conducted in the presence of the well water obtained on 10-25-83, 2-20-84, and 10-12-84. The isotherms are shown in Figure IV-34. A TCE isotherm conducted in organic-free water is included for comparison. All three isotherms conducted in the Wausau water showed a marked decrease from the single solute capacity. Although the 2-20-84 isotherm was conducted with a higher initial concentration, the isotherm shows a lower capacity than the other two isotherms. Higher initial concentration would decrease the difference between the single solute isotherm and the Wausau water isotherm. Therefore, the results shows that the adsorption capacity for a given compound will change seasonally as the background water matrix changes.

Because compounds will adsorb differently on different dates due to changes in the background concentration as shown in Figure IV-33,

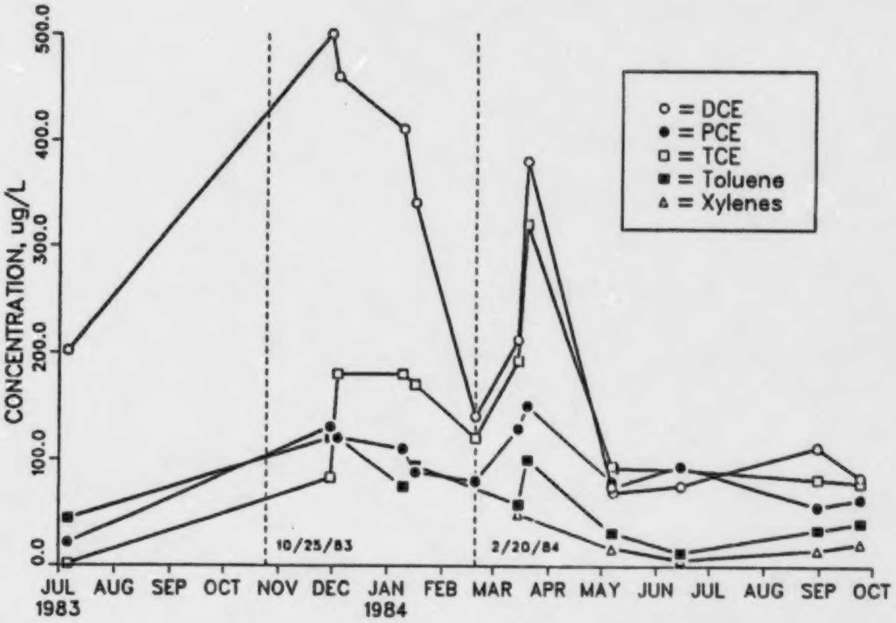

Figure IV-33. Concentration-History Profiles for Cis-1,2-Dichloroethene, Trichloroethene, Tetrachloroethene Toluene, and the Xylene Isomers from Well No. 4.

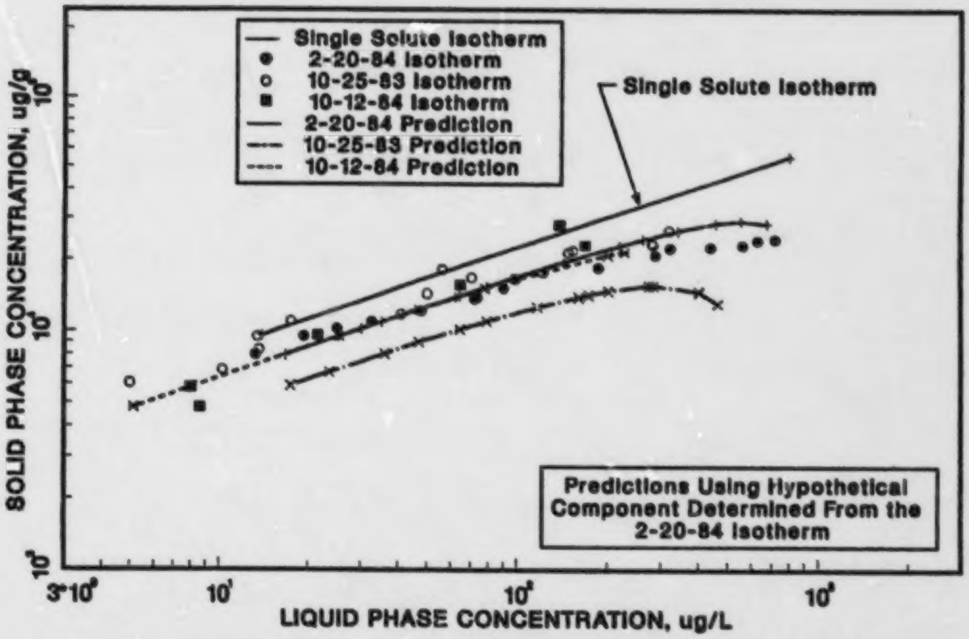

Figure IV-34. Trichloroethene Isotherm Data Conducted in Wausau Water on F-400 Carbon for Different Dates with the Prediction Based on the Hypothetical Component Determined from the 2-20-84 Trichloroethene Isotherm.

any hypothetical component found must be easily changed to take this background change into account. One possible way of doing this is to use the total concentration of VOCs as an indication of how the initial concentration of a hypothetical component will change.

Table IV-6 shows the concentrations of volatile organics found on the dates corresponding to three spiked TCE Wausau water isotherms. The concentrations were added and the initial concentration of the hypothetical component found for the 2-20-84 isotherm was adjusted by the ratios of total VOCs. The hypothetical components K, 1/n, and adjusted initial concentration were then used to predict the competitive effects of the Wausau water isotherms performed on 10-25-83 and 10-12-84. Figure IV-34 shows the predictions for all three dates. As can be seen, the predictions are quite far from the observed Wausau water isotherms, especially in the case of the 10-25-83 isotherm. The 10-25-83 isotherm may have an error in the initial concentrations of VOCs as discussed in Section IV-B, however, it seems that using the ratio of total concentration of VOCs will not predict the change in the hypothetical components initial concentration required to predict the adsorbing background strength on different dates.

D. COMPARISON OF COMPETITIVE EFFECTS USING CARBON THAT HAS BEEN PRESATURATED WITH PURGED WAUSAU WATER

During the course of operating a fixed-bed carbon adsorber, the weakly adsorbing TOC will migrate down the bed ahead of the strongly adsorbing VOCs due to chromatographic effects. The TOC background will then have the opportunity to pre-adsorb onto the carbon before the VOCs arrive. Two isotherm experiments were conducted in order to determine whether preadsorbing the TOC will have an impact on the adsorption of

Table IV-6. Hypothetical Components Used for Predicting the Adsorbing Background for Raw Water Isotherms Completed on 10-25-83 and 10-12-84 as Determined from the Hypothetical Component Found from the 2-20-84 Raw Water Isotherm.

	Concentration		
Component	2-20-84 μm/L	10-25-83 μm/L	10-12-84 μm/L
cis 1,2-dichloroethene	1.444	4.385	0.763
trichloroethene	0.914	0.472	0.517
tetrachlroethene	0.482	0.627	0.353
toluene	1.085	0.411	1.129
ethyl benzene	0.122	NA	0.048
o,p-xylene	0.278	NA	0.096
m-xylene	0.196	NA	0.063
TOTAL	4.521	6.613	2.251
Resultant Freundlich Parameters for the Hypothetical Component Found on 2-20-84			
K (μm/g)(L/μm)$^{1/n}$	336.8	336.8	336.8
1/n	0.2433	0.2433	0.2433
Initial Concentration	2.958	4.984	1.473

Note: The initial concentration of the hypothetical component found on 2-20-84 was multiplied by the ratio of total VOC concentrations to obtain the initial hypothetical component concentration for the other dates.

Note: The total concentration of DCE, TCE, PCE, and toluene for 2-20-84 is 3.925 μm/L. This was used to calculate the initial concentration of the hypothetical component for 10-25-83.

the VOCs. One TCE isotherm was conducted in Wausau water that was diluted with organic-free water by 31 percent of its original concentration. This was the control to show the effect of reducing the background concentration. Another TCE isotherm was conducted with carbon which was presaturated with purged Wausau water. The purging of the Wausau water was performed to remove the VOCs so that only the non-volatile TOC background is present. This would be similar to what would be expected in a fixed-bed adsorber. Presaturation was performed by placing the weighed amounts of carbon and 100 mL of purged well water into an isotherm bottle and equilibrating it for four days. Then 60 mL of Wausau water containing the VOCs and TOC background was added. The net result was a reduction in the VOC concentration by 62 percent. Figure IV-35 displays the results of both the diluted and presaturated isotherms along with TCE isotherms in organic-free water and Wausau water. The figure shows that diluting the Wausau water by 31 percent moves the Wausau water isotherm to the single solute isotherm line. Diluting the Wausau water isotherm by 62 percent with purged Wausau water moves the isotherm line over a very small amount. From this it can be said that the background TOC has a strong competitive effect when it is pre-adsorbed. Fettig (1984) has shown that preadsorbed TOC will slow down the rate of adsorption but will not affect the equilibrium for aliphatic compounds. Therefore, it seems that the 7-day equilibration time for the presaturated isotherm may have not been not long enough for equilibrium to be reached. It is interesting to note that Fettig found that preadsorbing TOC did affect the equilibrium for aromatic compounds. The TOC isotherm they completed was similar in capacity to what was found in this study.

E. TOTAL ORGANIC HALOGEN ISOTHERM COMPARISONS

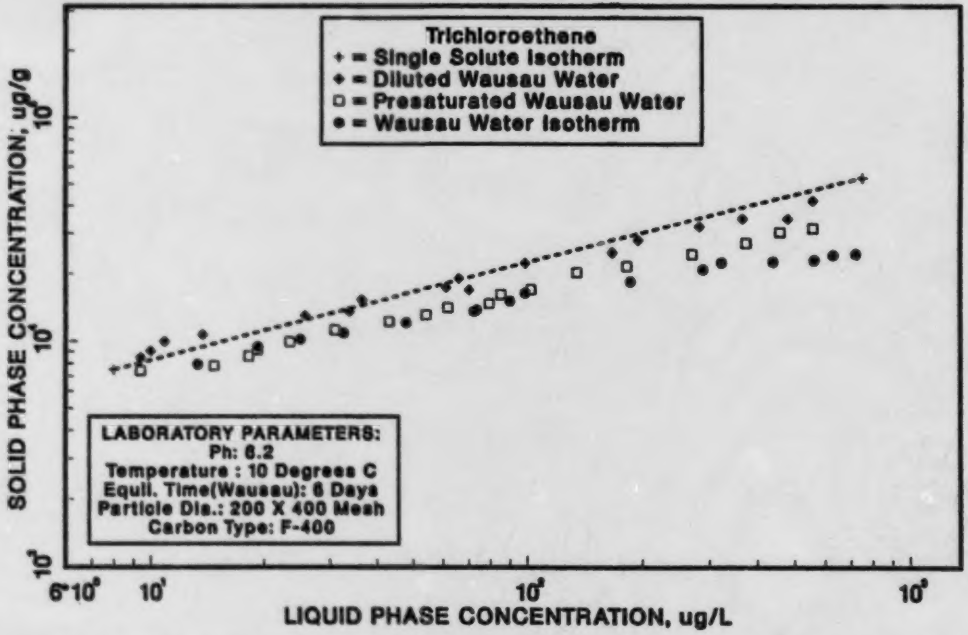

Figure IV-35. Isotherm Comparisons for Trichloroethene in Wausau Water, Diluted Wausau Water, Presaturated Wausau Water, and Organic-Free Water.

Figure IV-36 contains three total organic halogen (TOX) isotherms using Wausau water. One of the three isotherms is a dilution of another. Therefore, this isotherm is shifted slightly to the left of the other two. The two TOX isotherms which were not diluted seem to correspond. This indicates that the TOX portion of the Wausau water did not change drastically from December, 1984 to April 1985. Table IV-7 shows that the known chlorinated compounds can fully describe the TOX found in the Wausau water.

Also shown in Figure IV-36 is the solid and liquid-phase concentrations found in the pilot plant in Wausau, WI. The TOX data points for the pilot plant are very close to the TOX isotherm points.

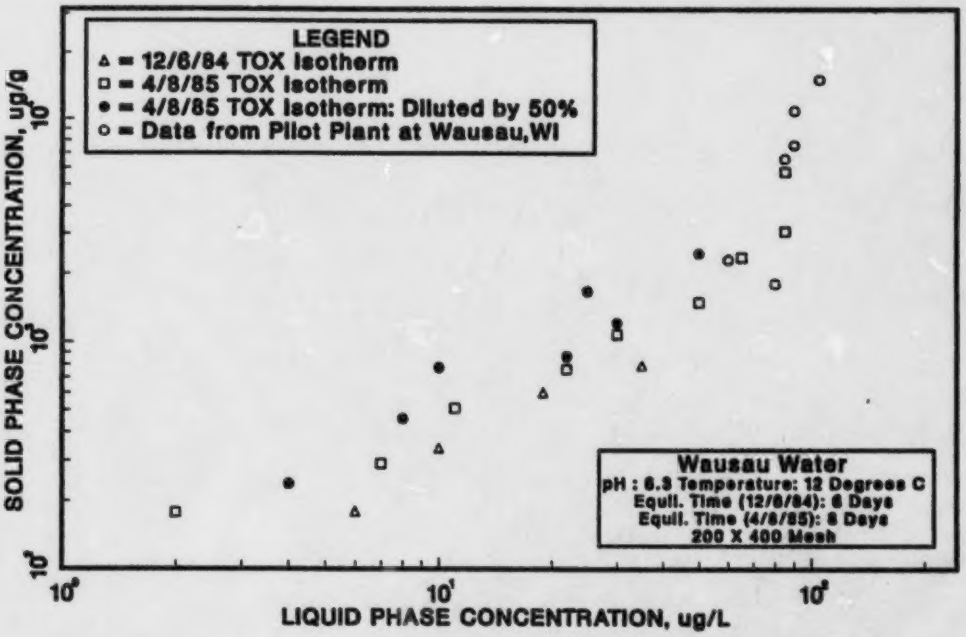

Figure IV-36. Total Organic Halogen Isotherms Completed in Wausau Water on F-400 Carbon with Data Obtained from the Pilot Column.

Table IV-7. Composition of Total Organic Halogen in the Wausau Water for 4/8/85.

Compound	4/8/85 Concentration µg/L	Calculated Concentration µg Cl^-/L	Percentage of Total
cis-dichloroethene	70.7	51.7	42.2
trichloroethene	34.1	27.6	22.5
tetrachloroethene	36.2	31.0	25.3
vinyl chloride	20.6	11.7	9.5
III-trichloroethane	0.7	0.6	0.5
Totals	162.3	122.6	100.0
TOX Found in Wausau Water		118.0	96.2

V. THE USE OF EQUILIBRIUM THEORY TO EVALUATE MULTICOMPONENT COMPETITION IN FIXED BEDS

The equilibrium column model (ECM) is a fixed bed adsorption model that ignores mass transfer resistances. The proposed ECM uses ideal adsorbed solution theory to predict the competitive effects in multicomponent mixtures. The ECM can be used to determine the elution order of the adsorbates, the lowest carbon usage rate in multicomponent mixtures, and the highest overshoot concentrations. Also, the ECM can be used to reduce the number of components to be specified in mass transfer models as discussed by Crittenden _et al._ (1986), and Friedman (1984).

It is the aim of this section to clearly define the model, present the mathematical development, compare the results with single solute calculations and pilot plant data, and explain the practical applications of the model.

A. EQUILIBRIUM COLUMN MODEL FRAMEWORK

The ECM which assumes negligible mass transfer resistances was developed for a step-up influent following the development of DeVault (1943). As shown in Figure V-1, the bed is divided into zones of constant composition that expand and move down the bed as solute accumulates on the adsorbent. The interface between two zones is referred to as a front. The components, zones, and fronts are numbered from the beginning of the bed. For the ensuing development, components are numbered in order of decreasing adsorbability, and N is the number of components. Consequently, component one which is the strongest adsorbing component, is present in the first zone only and component two which is the second most strongly adsorbing component is present in zones 1 and 2 only. In general, component i will be present in zones 1

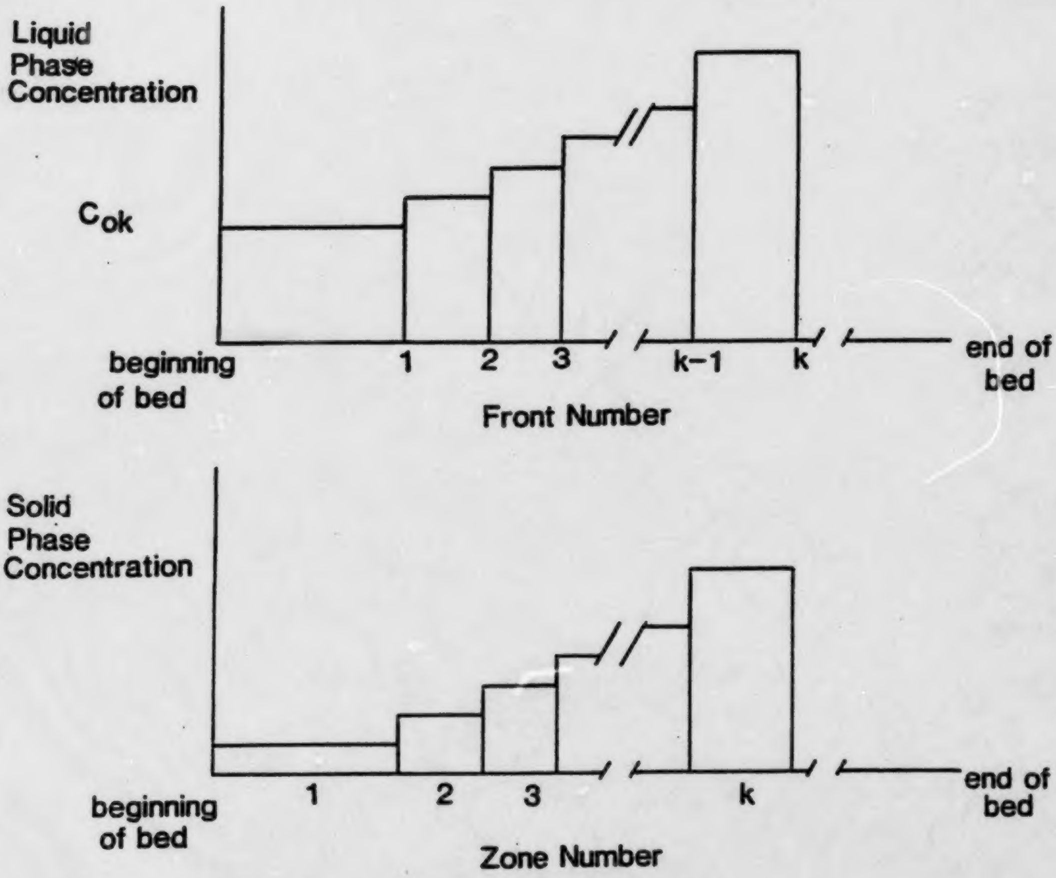
Liquid Phase Concentration
C_{ok}
beginning of bed
1
2
3
k−1
k
end of bed
Front Number
Solid Phase Concentration
beginning of bed
1
2
3
k
end of bed
Zone Number

Figure V-1. Representation of Column Profiles for Component k in the Equilibrium Column Model.

through i. For N components, zone i will contain components i through N, and zone N will contain only the weakest component, component N. To completely describe the ECM, equations must be developed to describe the velocity of the fronts and the concentrations in each zone.

B. MATHEMATICAL DEVELOPMENT AND METHOD OF SOLUTION

Incorporating the assumptions of equilibrium theory into a mass balance on wavefront k-1, as illustrated in Figure V-2, the following equation was derived to describe the liquid phase concentration for component i in zone k. This can only apply for components k through N.

$$C_{i,k} = \frac{(q_{i,k} - q_{i,k-1})\rho_B Vw_{k-1}}{(V_f - Vw_{k-1})\ \varepsilon} + C_{i,k-1} \qquad \text{(V-1)}$$

Where, $C_{i,k-1}$ is the liquid-phase concentration of component i in equilibrium with the solid-phase concentration $q_{i,k-1}$. ρ_B is the bulk density, V_f is the superficial fluid velocity, ε is the bed void fraction, and Vw_{k-1} is the velocity of the wave front between zones k-1 and k.

The wave velocity, Vw_k can be determined from a mass balance over the entire bed length at time t_k, where zone k just breaks through for component i.

$$Vw_k = \frac{V_f \varepsilon C_{oi} - \sum_{j=1}^{k-1} [(q_{i,j}\ \rho_B + C_{i,j}\varepsilon)(Vw_j - Vw_{j-1})] + (q_{i,k}\ \rho_B + C_{i,k}\varepsilon)Vw_{k-1}}{(q_{i,k}\ \rho_B + C_{i,k}\ \varepsilon)} \qquad \text{(V-2)}$$

Equations V-1 and V-2 combined with ideal adsorbed solution theory can describe the bed performance given the single solute Freundlich isotherm parameters, the initial concentrations for each component, the

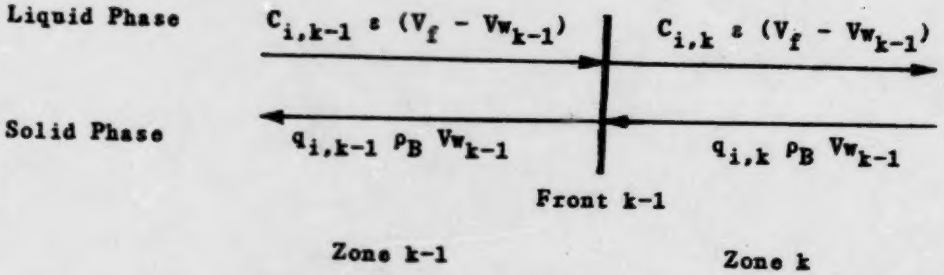
Liquid Phase
$C_{i,k-1}\ \varepsilon\ (V_f - Vw_{k-1})$
$C_{i,k}\ \varepsilon\ (V_f - Vw_{k-1})$
Solid Phase
$q_{i,k-1}\ \rho_B\ Vw_{k-1}$
$q_{i,k}\ \rho_B\ Vw_{k-1}$
Front k-1
Zone k-1
Zone k

Figure V-2. System Upon Which a Mass Balance on Front k-1 for Component i is written in the Equilibrium Column Model.

liquid loading to the bed, and the bed bulk density and porosity. All the overshoot concentrations and wave front velocities are determined starting in the first zone and progressing to the final zone.

In zone 1, the liquid-phase concentrations are at their initial values; therefore, only the solid-phase concentrations are unknown and can be calculated using IAST. Accordingly, there will be N equations and N unknowns. Equation V-3 is a simplification of the ideal adsorbed solution theory (IAST) equations developed by Fritz *et al.* (1981) and Crittenden *et al.* (1985) using the Freundlich isotherm expression. The limitations of this approach are discussed in *Crittenden et al.* (1985) and Jossens *et al.* (1978).

$$C_{i,1} = \frac{q_{i,1}}{\sum_{j=1}^{N} q_{j,1}} \left[\frac{\sum_{j=1}^{N} n_j \, q_{j,1}}{n_i \, k_i} \right]^{n_i} \qquad (i = 1, N) \qquad \text{(V-3)}$$

The velocity of the wavefront of zone 1 is obtained from Equation V-2 which reduces to the following equation:

$$Vw_1 = \frac{V_f \, C_{o1} \, \varepsilon}{(q_{1,1} \, \rho_B + C_{o1} \, \varepsilon)} \qquad \text{(V-4)}$$

For zone k (where k is greater than one), there are 2N - 2k - 2 equations and the same number of unknowns because components 1 through k-1 (which are more strongly adsorbed than component k), are only present in the earlier zones. Since both the $C_{i,k}$'s and $q_{i,k}$'s are unknown, Equation V-3 for zone k is combined with Equation V-1 to obtain the following equation expressed in terms of $q_{i,k}$ only.

$$\frac{q_{i,k}}{\sum_{j=k}^{N} q_{i,k}} \left[\frac{\sum_{j=k}^{N} n_j q_{j,k}}{n_i \; k_i} \right]^{ni} = \frac{(q_{i,k} - q_{i,k-1}) \rho_B Vw_{k-1}}{(V_f - Vw_{k-1}) \; \varepsilon} + C_{i,k-1} \qquad \text{(V-5)}$$

Equation V-5 is valid for components k through N and forms N - k - 1 simultaneous equations which are solved for the $q_{i,k}$'s. The liquid-phase concentrations $C_{i,k}$ are then calculated from Equation V-1, and the velocity with which wave i moves through the bed, Vw_k, is calculated from Equation V-2.

Once all the liquid and solid-phase concentrations have been determined, the maximum number of bed volumes fed to breakthrough and the carbon usage rate for component i can be determined using the following equations:

$$BVF_i = \frac{\sum_{k=1}^{N} [(q_{i,k}\rho_B + C_{i,k}\varepsilon)(Vw_k - Vw_{k-1})]}{Co_i \; Vw_i} \qquad \text{(V-6)}$$

$$\text{Usage Rate} = \frac{\rho_B}{BVF_i} \qquad \text{(V-7)}$$

The ECM equations are solved by a Newton-Raphson algorithm which was patterned after Crittenden et al., (1985) and by using ZSPOW from the International Mathematics and Statistics Library which solves sets of non-linear equations. The program was written in FORTRAN-77 and was run using a 8087 math co-processor. The software will run in 2 to 3 minutes for a seven component mixture on an IBM-PC. A more complete derivation of the equilibrium column model can be seen in Appendix X. The computer code can be seen in Appendix XI.

C. EQUILIBRIUM COLUMN MODEL PREDICTIONS

A comparison between the ECM predicted carbon usage rates, the single solute carbon usage rates evaluated at the influent concentration (which is in effect a single solute ECM prediction), and the summation of these single solute carbon usage rates is shown in Table V-1. The usage rates were calculated from Equations V-6 and V-7; consequently, the elution order is inversely proportional to the usage rate. The adsorbates and their influent concentrations in Table V-1 were obtained from the average influent concentrations of a pilot-scale fixed-bed adsorber located in Wausau, WI. These adsorbates and influent concentrations will be used throughout this section as an illustration. Since the ECM neglects mass transfer resistances, the usage rates calculated by the ECM will be the lowest possible. As shown in Table V-1, the single solute usage rates are not very close to the ECM predictions.

Another common method of determining usage rates is to sum the single solute calculated usage rates in succession from the strongest adsorbing to the weakest adsorbing. As shown in Table V-1, the usage rate which was determined by this method compares quite well to the ECM predicted values for the strongly adsorbing components, however, this is only coincidental. For the less strongly adsorbing compounds, such as TCE and DCE, the sum was much higher.

Table V-1. Comparison of Carbon Usage Rates of the Equilibrium Column Model to the Single Solute Usage Rates.

				Carbon Usage Rate (mg Carbon/L water)		
Adsorbate	Freundlich K $(\mu M/g)(L/\mu M)^{1/n}$	Freundlich 1/n	Influent Concentration (μg/L)	Single Solute Using Influent Concentrations		Equilibrium Theory
				Individual	Summation	
m-Xylene	1040	0.2458	5.2	0.098	0.098	0.156
o,p-Xylene	894	0.2587	9.2	0.184	0.282	0.268
Ethylbenzene	714	0.2953	4.5	0.151	0.433	0.394
Toluene	475	0.3282	19.3	0.737	1.170	1.204
Tetrachoroethene	435	0.3847	37.6	0.923	2.093	1.690
Trichoroethene	192	0.4328	47.9	4.02	6.11	2.94
cis-1,2 Dichoroethene	46.9	0.5562	70.9	20.4	26.5	18.6

Figure V-3 shows the breakthrough profiles obtained from the pilot plant study and the corresponding ECM prediction. Six empty bed contact times are shown on the figure. Also shown is the average influent concentration weighted over time, and the corresponding standard deviation concentrations in influent concentration. The model can be seen to predict the middle of the breakthrough profile and the highest overshoot concentration for DCE. Figure V-3 also demonstrates that as the empty bed contact time increases, the mass transfer zone becomes a smaller portion of the bed. Accordingly, for larger EBCTs, the pilot data approaches the ECM prediction. Therefore, the ECM may be able to accurately predict breakthrough profiles for full scale adsorbers which have very large empty bed contact times.

Figures V-4 and V-5 present the pilot plant breakthrough profiles, ECM predictions for TCE and PCE, and their influent concentration's standard deviations. Although it is difficult to determine if the ECM predicts the middle of the profile, it seems that this may be the case. However, this is difficult to evaluate because mass transfer has a greater impact on the breakthrough profiles for TCE and PCE.

Table V-2 shows the capacities found in the Wausau, WI pilot plant columns after one year of operation. The pilot column was built as a series of smaller beds. The capacities were found by integrating between the concentration profiles obtained from the sample ports between the beds. The empty bed contact times listed in Table V-2 are those of the sample ports at the beginning and end of each bed. Table V-3 shows the corresponding capacities that are predicted using the ECM after one year of operation. As shown in Tables V-2 and V-3, the ECM and the pilot column data cannot be compared directly, accordingly, the

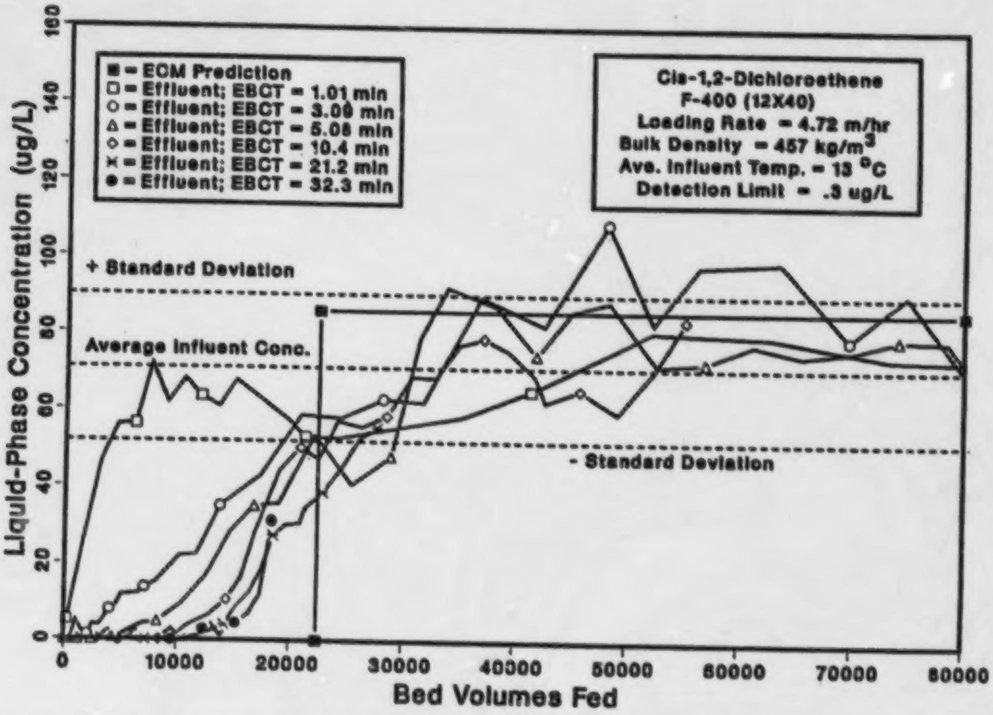

Figure V-3. Comparison of the Equilibrium Column Model Prediction to Concentration Profiles Obtained for Cis 1,2 Dichloroethene from a Pilot Scale Fixed Bed Adsorber Located in Wausau, WI.

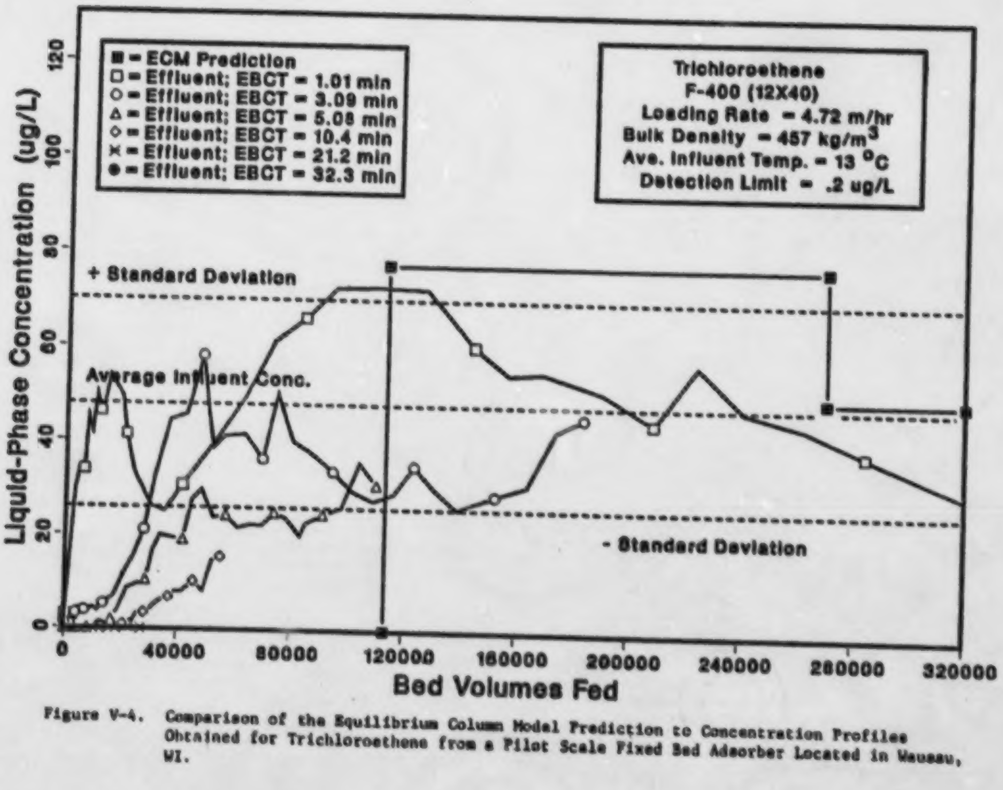

Figure V-4. Comparison of the Equilibrium Column Model Prediction to Concentration Profiles Obtained for Trichloroethene from a Pilot Scale Fixed Bed Adsorber Located in Wausau, WI.

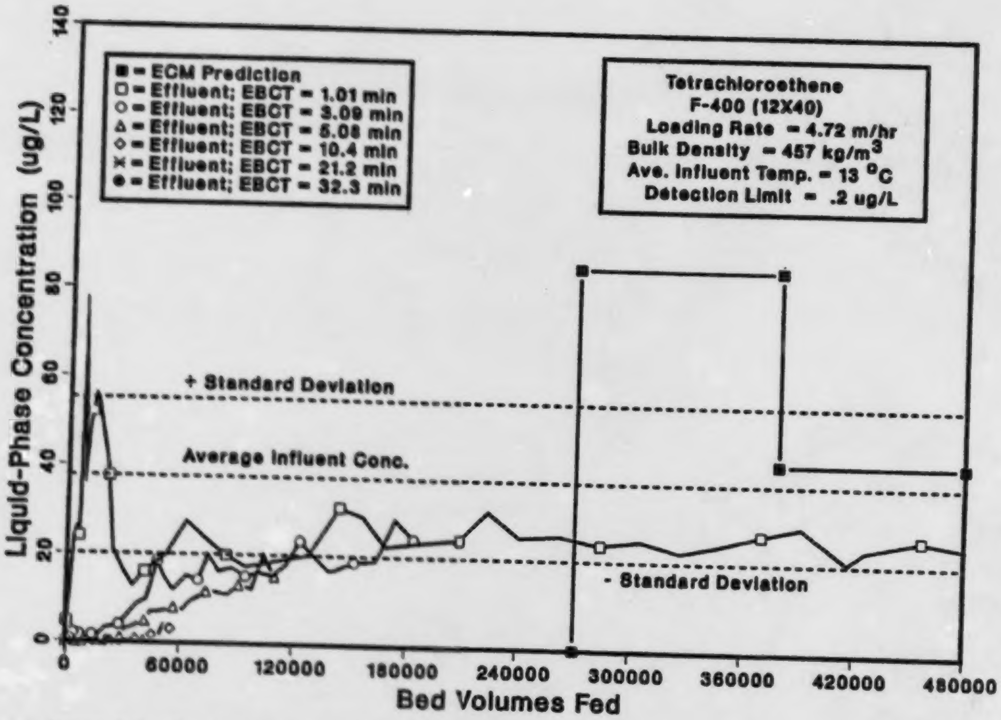

Figure V-5. Comparison of the Equilibrium Column Model Prediction to Concentration Profiles Obtained for Tetrachloroethene from a Pilot Scale Fixed Bed Adsorber Located in Wausau, WI.

Table V-2. Carbon Capacities for Volatile Organic Compounds for F-400 type Carbon as determined from Pilot Study in Wausau, WI.

Adsorbate		Carbon Capacities (mg/g) for Ranges of EBCTs (min)							
		Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Single Solute Isotherm	Raw$^\alpha$ Water Isotherm
	From:	0.0	1.01	3.09	5.08	10.4	21.2		
	To:	1.01	3.09	5.08	10.4	21.2	32.3		
cis,1,2-Dichloroethene	Pilot	2.82	0.75	4.27	2.70	5.27^*	3.10^*	3.82	1.85 to 3.80
	BCM	0.22	0.65	2.32	4.24	4.24	—		
Trichloroethene	Pilot	5.65	6.13	5.55^*	2.94^*	0.49^*	X^*	16.29	2.90 to 4.20
	BCM	1.72	13.57	$11.06^\#$	—	—	—		
Tetrachloroethene	Pilot	12.5	5.72^*	3.84^*	1.43^*	0.08^*	0.001^*	40.76	6.80 to 8.00
	BCM	12.6	$15.27^\#$	—	—	—	—		
Toluene	Pilot	11.8^*	2.65^*	1.23^*	1.46^*	0.004^*	X^*	26.20	
	BCM	16.1	$2.83^\#$	—	—	—	—		
Ethyl Benzene	Pilot	1.96	0.63^*	0.46^*	0.12^*	0.004^*	X^*	29.81	
	BCM	$4.82^\#$	—	—	—	—	—		
o,p-Xylene	Pilot	4.20^*	1.35^*	0.98^*	0.17^*	0.002^*	X^*	52.81	
	BCM	$9.68^\#$	—	—	—	—	—		
m-Xylene	Pilot	2.93^*	0.73^*	0.37^*	0.08^*	X^*	X^*	50.61	
	BCM	$5.28^\#$	—	—	—	—	—		

X = Carbon capacities are essentially zero.

* = The effluent concentration history profiles have not reached their influent values, indicating that the columns are not saturated.

# = The BCM prediction breaks through between the EBCT's which define the column. Hence, the column not saturated.

α = The initial isotherm concentrations for cis 1,2 dichloroethene, trichloroethene, and tetrachloroethene 70.7 to 56.2 µg/L, 34.7 to 23.7 µg/L, and 36.2 to 25.3 µg/L, respectively. The ranges are noted because the compounds degraded over the 7 day equilibration time of the isotherm. Since the concentrations varied, the capacities varied.

Table V-3. Carbon Capacities for Volatile Organic Compounds for F-400 Carbon as Determined from the Equillibrium Column Model.

Adsorbate	Carbon Capacities (mg/g) for Ranges of EBCTs (min)						
	Zone 1 0.0 to 0.16	Zone 2 0.16 to 0.28	Zone 3 0.28 to 0.41	Zone 4 0.41 to 1.26	Zone 5 1.26 to 1.77	Zone 6 1.77 to 4.21	Zone 7 4.21 to 21.4
cis,1,2-Dichloroethene	0.11	0.12	0.19	0.27	0.35	0.83	4.24
Trichloroethene	0.60	0.73	1.42	2.28	3.36	19.66	
Tetrachloroethene	3.33	4.17	9.35	17.43	53.74		
Toluene	2.59	3.43	9.56	23.53			
Ethyl Benzene	2.90	4.14	30.05				
o,p-Xylene	24.00	49.64					
m-Xylene	33.32						

results from the ECM in Table V-3 were averaged according to the percentage of the EBCT that would be contained in the pilot columns and those results are reported in Table V-2. By comparing the ECM and the pilot data in Table V-2, the ECM does a reasonable job in predicting the capacity in the pilot columns for the weakly adsorbing components such as dichloroethene for which the columns are saturated. However, for the stronger adsorbing compounds, such as m-xylene, the capacities calculated by the model are much higher than the observed capacity. Deviations between the ECM and pilot data can be attributed to mass transfer resistance and the time variable influent concentrations. It should also be noted that the inlet to the pilot plant contained an average total organic carbon concentration of 8.35 mg/L. This may have had an impact on capacity; even though, IAST predictions for dichloroethene agreed with the Wausau water isotherm data (Crittenden et al., 1986).

Table V-2 also shows the single solute and Wausau water isotherm capacities which were evaluated at the initial influent concentrations. The single solute isotherm capacity for DCE is close to what was found in the pilot plant. The other components, however, have single solute isotherm capacities which are much higher than those found in the pilot column. The reason for this is that DCE is a weakly adsorbing component which travels down the column faster than the stronger adsorbing components. Therefore, the DCE has few background components to compete for adsorption sites with, and hence, behaves as a single solute. The other components which are more strongly adsorbed are located in the early part of the column where there are many background components to compete for adsorption sites and the resultant capacities are lower.

In order to obtain the capacities from the Wausau water isotherms, each isotherm was extrapolated to its average initial concentration in the Wausau water. Extrapolating these isotherms to their initial concentrations will cause large errors with respect to the capacities that are obtained because multicomponent isotherm capacities decrease as the initial concentrations is approached. This is because the carbon dosages are smaller as the isotherm approaches its initial concentration and less adsorption sites will be available for the weaker adsorbing components to occupy. The initial isotherm concentrations for cis 1,2-dichloroethene, trichloroethene, and tetrachloroethene were between 70.7 and 56.2 µg/L, 34.7 and 23.7 µg/L, and 34.1 and 25.3 µg/L, respectively. It can be seen in Table V-1 that these concentrations do not correspond to the average influent concentrations of these components. Therefore, the isotherm which was performed will deviate from a raw water isotherm where the average influent concentrations are used, and there will be large errors between the capacities involved. In addition, the multicomponent isotherms were conducted in sealed bottles where the dosage of carbon is exposed to a fixed mass of the adsorbates, whereas; in the column, the dosage of carbon is exposed to a increasing mass of the adsorbates which undergo chromatographic separation. Therefore, if the carbon capacities observed in the pilot plant are equal to the multicomponent isotherm capacity, it is only by coincidence, and not because the same competitive effects are taking place.

The overshoot concentrations can be used to describe the breakthrough of a component without requiring all the components in the water matrix to be represented. This is important because computer programs that incorporate mass transfer often become unreasonably slow if a large number of components are used. Models which incorporate mass transfer are discussed in Crittenden _et al._ (1980), Thacker (1981), Thacker _et al._ (1981), Friedman (1984), and Crittenden _et al._ (1986). The problem can be avoided by taking the overshoot concentrations of an intermediate zone, as calculated by the ECM, and use them for the influent concentrations in the mass transfer model. This will eliminate the stronger adsorbing compounds found in the earlier zones and works well if mass transfer does not spread out the strongly adsorbing components. Sontheimer _et al._ (1985) has shown that this method will accurately predict the breakthrough for total organic carbon. Friedman (1984) and Crittenden _et al._ (1986) demonstrated that a six component model could be reduced to a three component model using the proposed technique. Table V-4 shows the results of using the overshoot concentrations of an intermediate zone as influent concentrations to the ECM. This is compared to a seven component ECM run using the pilot plant influent concentrations which was used to find the overshoot concentrations. The results show that this method works well in predicting the bed volumes fed to breakthrough for the remaining two components. In this case, the overshoot concentrations from zone 6 obtained from the ECM were used as initial concentrations in the ECM. Because the ECM program runs quickly even for seven components, this is of no advantage except to show that the number of components needed to be specified can be reduced for mass transfer models. This is only true as long as the mass transfer zones of the strongly adsorbed components do not significantly overlap the weakly adsorbed components (Friedman 1984, Crittenden _et al._ 1986).

Another useful feature of the ECM is that it may be used to lump

Table V-4. Equilibrium Theory Results Using Overshoot Concentrations as Influent Concentrations to Reduce the Number of Components Needed to be Specified.

Influent Concentrations C_o (μg/L) / Bed Volumes Fed to Breakthrough (BVF)

Adsorbate	7 Component Run Using Pilot Plant Influent Concentrations for the Influent Concentrations		Two Component Run Using Overshoot Concentrations from Zone 6 of the 7 Component Component Run for Influent Concentrations		2 Component Run Using Pilot Plant Influent Concentrations for Influent Concentrations	
	C_o (μg/L)	BVF	C_o (μg/L)	BVF	C_o (μg/L)	BVF
m-Xylene	5.2	2928000	—	—	—	—
o,p-Xylene	9.2	1705000	—	—	—	—
Ethylbenzene	4.5	1161000	—	—	—	—
Toluene	19.3	379500	—	—	—	—
Tetrachloroethene	37.6	270700	—	—	—	—
Trichloroethene	47.9	113600	77.3	116200	47.9	151200
cis,1,2-Dichroroethene	70.9	22400	71.9	22690	70.9	23290

the competitive effects of complex mixtures into fewer components. This is useful from an experimental point of view because one may be interested in which component and what concentration from a class of components may be spiked into a water to represent the competitive interactions of the class of compounds. The procedure is to add the molar concentrations of the components that are to be combined to form one consolidated component. The ECM program is then run with the consolidated component in place of the individual components that it represents. The consolidated component takes on the Freundlich parameters of one of the individual components. By comparing the ECM results with the consolidated component to those with the original mixture, one can decide which component and if necessary the influent concentration of the consolidated component that are required to represent the competitive interactions of that class of compounds. Table V-5 shows the results of this procedure. In this example, one component from the substituted benzenes, m-xylene, o,p-xylene, ethylbenzene, and toluene, was to be chosen to give the same competitive effect as these four components. The initial concentrations were then added together, and the Freundlich parameters of Toluene were used to represent the competitive interactions of the substituted benzenes. As shown in Table V-5, the bed volumes fed to breakthrough for the three remaining compounds were more accurately predicted by this procedure than the results with the four components using the pilot plant influent concentrations. Although the results in Table V-5 are not that dramatic, this procedure has been used to plan a spiking experiment in which 50 components were represented by 6 components (Hilton and Mahachek, 1986).

Table V-5. Equilibrium Theory Results Found By Combining Similar Zones to Reduce the Number of Components Needed to be Specified.

	Influent Concentrations (C_o) / Bed Volumes Fed to Breakthrough (BVF)					
Adsorbate	7 Component Run Using Pilot Plant Influent Concentrations for Initial Concentrations		4 Component Run Combining m-Xylene, o, p-Xylene, Ethylbenzene, and Toluene into one Zone		4 Component Run Using Pilot Plant Influent Concentrations for Initial Concentrations	
	C_o (μg/L)	BVF	C_o (μg/L)	BVF	C_o (μg/L)	BVF
m-Xylene	5.2	2928000	Combined Component: as Toluene		—	—
o,p-Xylene	9.2	1705000			—	—
Ethylbenzene	4.5	1161000	Combined Component: as Toluene		—	—
Toluene	19.3	379500	35.8	351800	19.3	485200
Tetrachloroethene	37.6	270700	37.6	276100	37.6	332600
Trichloroethene	47.9	113600	47.9	114600	47.9	121100
cis-1,2 Dichloroethene	70.9	22400	70.9	22430	70.9	22610

D. SUMMARY

For designing fixed bed adsorbers, the ECM will predict the elution order of the adsorbates, the lowest carbon usage rate in multicomponent mixtures, and the highest possible overshoot concentrations. It can also be used to reduce the number of components to be specified in models which take mass transfer into account. In addition, the ECM program runs quickly and requires only the influent concentrations and the Freundlich parameters for the components present in the water matrix. The fact that it takes multicomponent interactions into account makes it a superior method for determining carbon usage rates as compared to using single solute calculations evaluated at the influent concentrations.

VI. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1.) The Polanyi Adsorption Potential Theory gives good approximations of single solute isotherms given the solubility, density, and molecular weight of the solute in question.

2.) Urano's modified Freundlich approach, the Clausius-Clapeyron equation, and the Polanyi adsorption potential theory predicted the effect of temperature on isotherms in the same manner.

3.) Multicomponent adsorption of VOCs in the Wausau groundwater was accurately predicted in most cases by ideal adsorbed solution theory assuming the VOCs to be the adsorbing background and ignoring the total organic carbon.

4.) The hypothetical components found by fitting a tracer isotherm was used with good success in predicting the adsorbing background for the Wausau, WI groundwater. However, the hypothetical components found by fitting a total organic carbon isotherm did not predict the adsorbing background for the Wausau, WI groundwater.

5.) The Equilibrium Column Model can be used to predict the elution order of the adsorbates, the lowest carbon usage rate in multicomponent mixtures, and the highest overshoot concentrations. Also, it can be used to reduce the number of components to be specified in models which incorporate mass transfer.

6.) Urano's modified Freundlich approach is not able to predict single solute isotherms.

Recommendations for Future Work

1.) Conduct single solute isotherm studies from very low concentrations up to solubility in order to better define the

Polanyi potential correlation curve and to determine the concentration range where the Freundlich equation is valid.

2.) Conduct single solute isotherms at various temperatures to determine the effect of temperature on isotherms. The applicabiltiy of the Urano's modified Freundlich equation, the Clausius-Clapeyron equation, and the Polanyi potential adsorption theory as discribed in this thesis should be determined.

3.) Apply the Net Adsorption Energy Method (NAEM) to correlate single solute isotherms. Compare this to the Polanyi adsorption potential theory.

4.) Determine hypothetical components found by fitting a tracer isotherm of a natural groundwater, and perform rate studies to determine the hypothetical components rate parameters for use in mass transfer column models to predict breakthrough profiles for solutes.

5.) Determine a universally tested and acceptable method means for predicting solubilities for use in the correlations discussed in this thesis.

APPENDIX I. NOMENCLATURE

a = Coefficient used to describe adsortion (t^2/L^2)

A = Coefficient used to describe adsorption ($Mt/L^2/M$)

a_{org} = Activity of the organic solute in the water

A_b = Cross sectional area of bed (L^2)

B = Slope of correlation curve

C = Liquid phase concentration (M/L^3)

Co = Initial liquid-phase concentration (M/L^3)

C_s = Solubility (M/L^3)

C_t = Total molar concentration (M/L^3)

K = Freundlich constant $(M/M)(L^3/M)^{1/n}$

k' = Modified Freundlich constant ($M/M/t$)

K_a = Reaction term constant $\{Products\}/\{Reactants\}$

L = Length

M = Mass

MW = Molecular weight

N = Normalizing factor for Polanyi potential theory

$1/n$ = Freundlich constant (dimensionless)

q = Solid phase concentration (M/M)

Q = Flow rate (L^3/t)

Q_{iso} = Isosteric heat of adsorption (L^2/t^2)

t = Time

T = Temperature

V = Molar volume of solute (L^3/M)

V_f = velocity of front (L/t)

Vm = Volume of zone (L^3)

Vw = velocity of wave (L/t)

W = Volume adsorbed (L^3/M)

W_o = Maximum volume adsorbed (L^3/M)

X = Mole fraction

Greek

α = Refractive index function (dimensionless)

γ = Abscissa scaling factor (dimensionless)

γ^{∞}_{aq} = Activity coefficient at infinite dilution

ε = Bed void fraction (dimensionless)

ε_{eq} = Adsorption potential (L^2/t^2)

η = Refractive Index (dimensionless)

λ = Abscissa scaling factor (dimensionless)

ρ = Density (M/L^3)

ρ_B = Bulk density of bed (M/L^3)

σ = Surface tension (ML^2/T^2)2

ω = Power to which the correlation curve is fit.

SUBSCRIPTS

i = Compound

j = Compound

k = Zone

l = Solvent

s = Solute

Abbreviations

BVF = Bed Volumes Fed to Breakthrough

DCE = Cis 1,2-dichloroethene

ECM = Equilibrium Column Model

ET = Equilibration Time

F-400 = Calgons Filtrasorb F-400 carbon

GAC = Granular Activated Carbon

PCE = Tetrachloroethene

TCE = Trichloroethene

TOC = Total Organic Carbon

TOX = Total Organic Halogen

WV-G = Westvaco activated carbon

APPENDIX II. REFERENCES

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APPENDIX III. PROCEDURE FOR BOTTLE POINT ISOTHERM STUDIES

By Paul Luft, David Perram, Thomas Speth, and David Hineline

The following is a step by step procedure for conducting an isotherm experiment. Randtke and Snoeyink (1983) and Crittenden and Hand (1983) discuss some of the important considerations that should be addressed when conducting an isotherm experiment. Consult these papers for additional details.

I. Trace Organics Cleaning Procedure

All equipment that comes in contact with the carbon must be cleaned by the following procedure.

a) First, all equipment is to be washed with Micro, a phosphate free laboratory cleaner.

b) Second, rinse with Milli-Q water several times and then air dry. The Milli-Q water system consists of:

  i) Two activated, adsorption cartridges to remove dissolved organics.

  ii) Two ion exchange cartridges to remove cations, anions and ionized organics.

  iii) A one meter GAC packed column.

  iv) A millipore membrane filter to remove microorganisms greater than 0.45 um.

c) Rinse with methanol and air dry.

d) All glassware should be baked in an oven at 250°C for one hour. All teflon and stainless steel apparatuses should be dried for one hour at 105°C in a forced air oven.

II. Preparation of Powdered Carbon

The carbon to be used should be the same as that used in related experiments.

1. Procedure for Washing Granular Carbon

   a) Place granular carbon to be washed in clean glass beakers or on a sieve with openings such that the smallest required particle size does not pass through.

   b) Rinse with Milli-Q water several times to remove fines. Keep rinsing until the supernatant is clear.

   c) Dry thin layers of the carbon slurry overnight (16-20 hrs) in glass screw cap bottles at 105°C with a slow helium purge to prevent any contamination present in the gas phase surrounding the drying carbon. Cool in a desiccator.

   d) Store carbon in air-tight, borosilicate, dark glass bottles in the dark until used.

2. Preparation of Powdered GAC for Isotherms

   a) Separate an adequate amount of carbon from the cleaned granular carbon to perform all the necessary isotherms.

   b) Completely crush all the carbon to be used for the isotherm experiments to a 200x400 (US std.) sieve size using a suitable carbon crushing procedure.

   c) Place the powdered carbon in isotherm bottles so that they are approximately 1/3 full. Fill the remaining volume with Milli-Q water and shake for a few minutes, then centrifuge each bottle for at least 1/2 hour at 2300 rpm.

   d) Pour off supernatant. This will remove the fine suspended particles that may interfere with the final isotherm analysis.

e) Place the isotherm bottles containing the carbon in the oven at 105°C overnight (16-20 hrs) with a slow helium purge. Cool in a desiccator.

f) Store carbon in airtight, borosilicate, dark glass bottles in the dark until ready to use.

3. Calculations Procedure for Determining Carbon Dosages

a) Obtain preliminary isotherm data upon which to base the dosages. Preliminary isotherm data can be obtained from literature or calculated by running a preliminary isotherm using a relatively high C_o and a wide range of carbon dosages (at least 5). Plot log C vs. log q to determine K and 1/n according to the Freundlich Isotherm Equation.

$$q = KC^{1/n} \tag{VII-1}$$

The Polanyi Potential Theory can be used to estimate isotherm data. A procedure for the calculation is shown in Section II-4.

b) To obtain C_o, use the highest C, the lowest measurable carbon dosage (Mettler balance 1 mg), and an estimate of the range of C desired in the following equation.

$$C_o = C\,[MKC^{1/n}]/V \tag{VII-2}$$

in which, K and 1/n are determined in item a or by the procedure for estimating isotherms, M is minimum carbon dosage, and V is volume of isotherm bottle

c) Determine carbon dosages to cover range from lowest measurable dosage to lowest measurable liquid concentration. For a given liquid concentration (C) the carbon dosage can be calculated from a mass balance on the isotherm bottle.

$$M = V[C_o - C]/[KC^{1/n}] \qquad \text{(VII-3)}$$

Calculate dosages such that the log C's are evenly spaced.

4. Procedure for Estimating Isotherms.

The Polanyi potential method as discussed in Section III-B-2 of this thesis can be used to estimate isotherms of compounds knowing their molecular weight, density, and solubility. The procedure for the calculation is completed below.

a) For application, the correlation curve must first be determined for one or more known isotherms. The volume adsorbed is calculated by the following equation.

$$W = Q \;/\; \rho \;/\; 10^6 \qquad \text{(VII-4)}$$

in which, W is the volume adsorbed in ml/g; Q is the solid phase concentration of the isotherm in μg/g; and ρ is the density of the solute in g/ml. The volume adsorbed is calculated for each isotherm data point, as is the adsorption potential over molar volume which is calculated in the following equation.

$$\varepsilon \;/\; V = \frac{RT \ln\,(C_s/C)}{MW/\rho} \qquad \text{(VII-5)}$$

in which, ε is the adsorption potential in cal/gmol; V is the molar volume of solute in ml/gmol; R is the ideal gas constant 1.987 cal/gmol/^{o}K; T is the temperature in ^{o}K; C_s is the solubility of the solute in μg/L; C is the liquid phase isotherm concentration in μg/L; MW is the molecular weight of the solute; and ρ is the density of the solute in g/ml.

b) Once the volume adsorbed and the adsorption potential over molar volume has been calculated for each isotherm point, they are plotted as the natural log of the volume adsorbed versus adsorption potential over molar volume as discribed earlier, the data is then fit to the following equation.

$$\ln W = B\ (\varepsilon/V)^{\omega} + \ln W_o \qquad \text{(VII-6)}$$

From work completed in this thesis it was found that for F-400 carbon the constants B, ω, and W_o are −0.02766, 1.2083, and 0.6299, respectively. For WV-G carbon, B, ω, and W_o were found to be −0.9458, 1.0, and 1.0940, respectively. For BPL carbon, B, ω, and W_o was found to be −0.06124, 1.0, and 0.1518, respectively. The above numbers were found using liquid phase isotherms; no gas phase isotherms were used. If the data, when fitted, has a value of ω less than one, it should be fitted using σ equal to one (a straight line).

c) After the correlation curve is defined, the solid phase concentration can be calculated for any given liquid phase concentration for any hydrophobic compound. This can be done with the following equation.

$$Q = 10^6 * \rho * \exp\left[B * \left[\frac{R*T*\ln(C_s/C)}{MW / \rho} \right]^{\omega} + \ln W_o \right]$$

(VII-7)

where the variables are the same as declared before.

d) From the calculated solid and liquid phase concentrations, Freundlich K's and 1/n's can be calculated. A computer program which uses the Polanyi potential theory to determine Freundlich K's and 1/n's is shown in Appendix VI.

5. Procedure for Weighing of the Powdered Carbon

This procedure allows the carbon to be handled at ambient conditions by calculating a correction for adsorbed water from the air.

a) Let carbon come to equilibrium with ambient conditions taking care not to expose it to organic vapors.

b) Weigh out a sizable amount of carbon (at least 100 mg.) in a tared bottle. This is based on the adsorption of 1% water by weight from the atmosphere.

c) Dry for 2 hours at 105°C, cool in a desiccator. Using a tared cap, seal the bottle and weigh.

d) Calculate the percentage change in carbon weight from the carbon at equilibrium with air and the dry carbon. Use this as a correction factor for the weighed carbon dosages of carbon by difference using weighing paper. Use lint free laboratory weighing gloves for weighing and be careful not to weigh fingerprints. Correct for ambient conditions, and place in pre-labeled isotherm bottles.

III. Solution Preparation and Handling

1. Preparation

a) Use Milli-Q water or the background water of interest to conduct the isotherms. If biological growth is a problem in the water matrix, autoclave the solution for 20 minutes at 121°C (15 psig). Autoclaving can cause significant changes in the background water, for example, loss of VOCs. Cool to room temperature.

b) Use a clean container (glass, stainless steel, or teflon with teflon floating cover) as the isotherm solution delivery container, such that its volume is at least 30% more than necessary to do isotherms. See Figure VII-1.

c) Add the water matrix which is to be used and buffer to desired pH. For pH of 6, a 10^{-3} phosphate buffer is used. 1 ml of a 1 M Potassium Monobasic Phosphate solution is added to a liter of solution and the pH is adjusted to 6.0 using 1N NaOH solution. Note that some water matrices may not need to be buffered due to its own buffering capacity.

d) Prepare a concentrated stock solution of the chemical(s) in Milli-Q water. This may be accomplished by injecting the pure solute(s) into a 45 ml vial containing Milli-Q

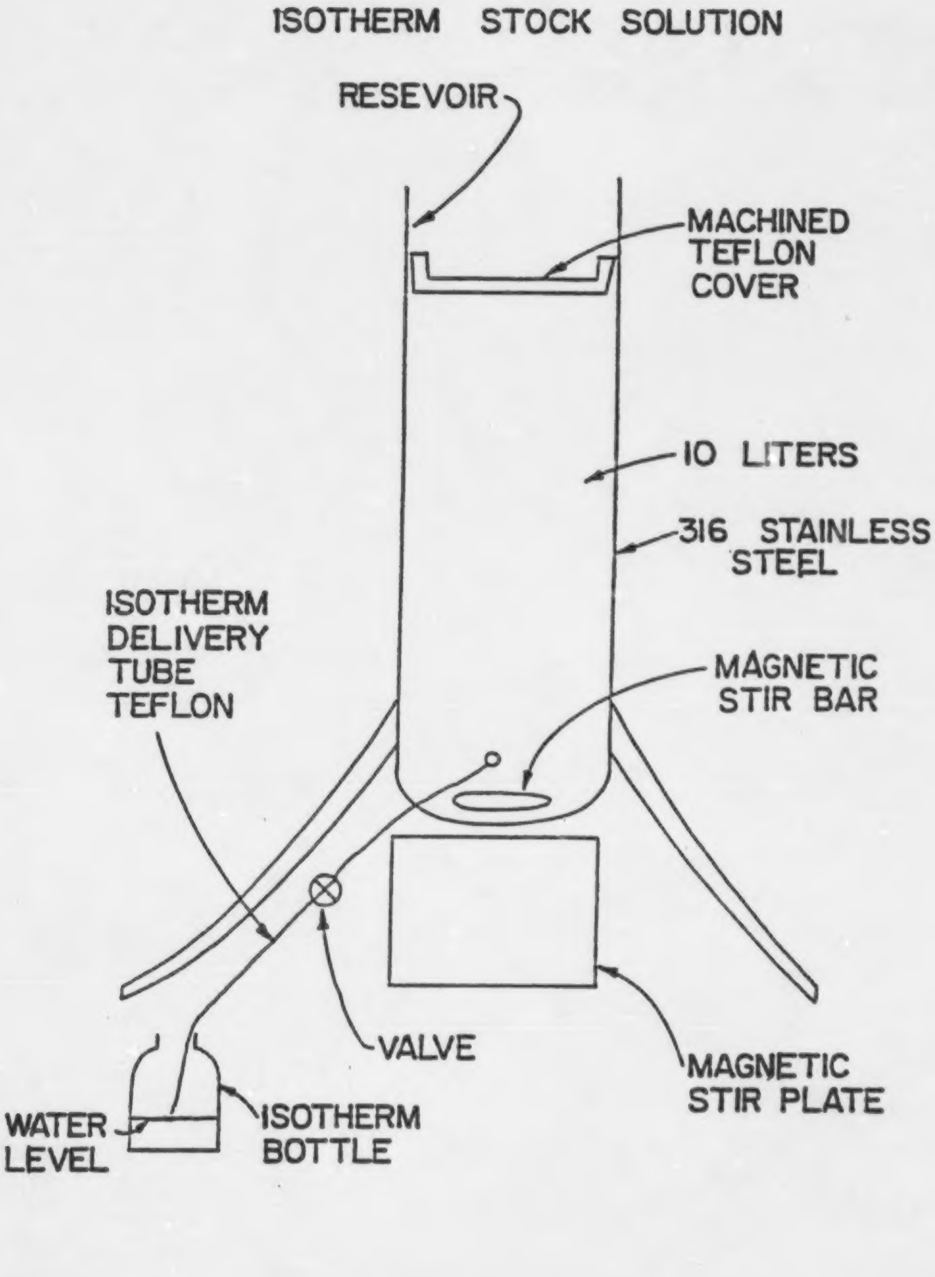
ISOTHERM STOCK SOLUTION
RESEVOIR
MACHINED TEFLON COVER
10 LITERS
316 STAINLESS STEEL
ISOTHERM DELIVERY TUBE TEFLON
MAGNETIC STIR BAR
VALVE
MAGNETIC STIR PLATE
WATER LEVEL
ISOTHERM BOTTLE

Figure VII-1. Schematic Diagram of the Isotherm Delivery Apparatus.

water and continue mixing the vial until the solute(s) are completely dissolved.

e) Spike the water in the isotherm delivery container with the stock prepared in step (d) and insert floating cover to prevent volatilization.

f) Using a teflon stir bar, completely mix the solution. To determine if solution is mixed, take samples from the teflon tube every 15 minutes until concentration does not vary. Let solution become stagnant before filling isotherm bottles.

2. Bottle Filling

Do not begin bottle filling procedure until carbon dosages have been weighed and placed in bottles.

a) Attach a teflon tube to the spigot near the bottom of the delivery container. (See Figure VII-1.)

b) Use a valve on the end of the teflon tube to control flow.

c) Fill an empty initial concentration bottle at the beginning, middle and end of the isotherm bottle procedure, in addition, fill a blank bottle at the beginning, end, and after every three isotherm bottles. (e.g., 12 isotherm bottles; C = initial concentration bottle, B = blank bottle, S = isotherm point; the order of filling would be C,B,S,S,S,B,S,S,S,B,C,S,S, S,B,S,S,S,B,C)

d) Use a procedure to fill bottles that causes the least amount of agitation of the solution. The teflon tube should not be allowed to come into contact with the solution in the isotherm bottle since carbon will cling to the teflon tube and change the dosage. To prevent loss of carbon from the isotherm bottle when capping, fill the bottle so that the edges of the concave miniscus just touch the bottle lip.

IV. Equilibration

a) The time to equilibrium is dependent on the particle size, dosage of carbon, and the surface diffusivity of the solute. Consult the paper by Crittenden and Hand (1983) for a thorough discussion of equilibration time.

b) It is recommended to run the isotherms for a much longer period than that calculated in (a). Equilibration of 5 to 7 days is common for synthetic organic chemicals.

c) Place isotherm bottles in a tumbler at 25 rpm and be sure the temperature is controlled until equilibrium is achieved.

d) Centrifuge bottles 30 min at approximately 2,000 rpm to settle carbon.

e) Remove cap and analyze according to analytical procedure.

APPENDIX IV - ISOTHERM DATA SHEETS

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol.,ml = 160** **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.0

Chemical: Cis-Dichloroethene **Initial Conc.,ug/L:** 1733±150

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 7.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	3.19	1340.0	19600
5	5.74	1140.0	16500
6	7.47	1080.0	14100
7	9.28	900.0	14400
8	11.58	762.0	13400
10	12.94	676.0	13100
11	14.43	673.0	11700
12	16.66	578.0	11100
13	19.00	547.0	9990
14	21.43	450.0	9580
17	24.00		
18	26.07	379.0	8310
19	27.69	355.0	7960
20	30.64	300.0	7480
21	31.81	304.0	7190
23	31.58	311.0	7200
24	38.07	247.0	6240
25	40.30	223.0	6000
26	42.91	211.0	5680
27	61.88	143.0	4110

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	1470.0
	15	1840.0
	30	1830.0
Equilibrated Blanks		
	2	1760.0
	3	1820.0
	9	1620.0
	16	1780.0
	22	1940.0
	28	1750.0
	29	1520.0

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc., ug/L:** 529.0 ± 13.6

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 6.5

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	30.95	--*	--
4	28.52	--*	--
5	26.44	--*	--
6	24.11	--*	--
8	21.80	--*	--
9	20.22	--*	--
10	17.02	--*	--
11	15.13	--*	--
14	13.11	5.3	6400
15	11.51	7.6	7250
16	10.38	9.4	8020
17	8.28	15.2	9940
19	6.40	29.2	12500
20	5.49	35.3	14400
21	4.27	53.9	17800
22	2.16	174.8	26300
23	1.27	269.4	32800
25	1.32	283.1	29900
26	2.76	119.5	23800

Immediately Extracted Blanks:	I.D.	C_o, ug/L
Equilibrated Blanks	1	557.0
	2	524.0
	7	506.0
	12	519.0
	13	540.0
	18	538.0
	24	520.0
	27	525.0
	28	539.0
	29	526.0

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*Concentration too low for accurate measurement.

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature,°C:** 10 ± 1 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc.,ug/L:** 550 ± 8

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 3

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3M1	34.97	0.9*	--
4M1	27.98	5.9	3110
5M1	21.87	3.7*	--
6M1	19.33	4.0*	--
8M1	14.22	5.8	6130
9M1	19.21	4.5	4540
10M1	16.71	5.8	5210
11M1	16.08	5.2	5420
13M1	11.48	10.4	7520
14M1	10.01	12.6	8590
15M1	9.34	16.6	9140
16M1	7.50	24.8	11200
17M1	6.81	33.3	12140
19M1	5.91	39.2	13840
20M1	5.05	57.0	15630
21M1	3.91	88.3	18900
24M1	2.84	157.5	22120
25M1	2.33	229.5	22020
27M1	1.64	290.5	25340
28M1	1.00	402.5	23630

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1M1	547.5
	12M1B	552.2
	31M1	550.6
Equilibrated Blanks	2M1	541.2
	7M1	537.8
	12M1	558.4
	18M1	543.5
	26M1	561.0
	30M1	559.5
	22M1	552.1

*Data points not used due to concentrations too low for accurate measurement.

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0 x 10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.0

Chemical: Tetrachloroethene **Initial Conc., ug/L:** 2732 ± 36

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 6

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	1.13	914.6	257400
5	2.39	462.6	151900
6	1.33	833.8	228400
7	2.69	381.5	139800
8			
10	3.56	243.1	111900
11	4.14	170.1	99030
12	4.60	142.9	90070
13	5.31	105.2	79160
14	6.59	75.1	64520
17	7.15	59.1	59820
18	7.54	58.9	56730
19	9.34	44.4	46050
20	10.81	27.9	40030
21	11.69	19.2	37140
23	13.25	14.3	32820
24			
25	18.34	10.1	23750
26	20.72	7.1	21040
27	23.82	8.0	18300

Immediately Extracted Blanks:	I.D.	C_o, ug/L
	1	2725.5
	15	2766.2
	30	2694.6
Equilibrated Blanks	2	2786.7
	3	2740.7
	9	2736.4
	16	2741.5
	22	2748.0
	28	2727.0
	29	2657.1

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0x10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.0

Chemical: Cis-Dichloroethene **Initial Conc., ug/L:** 1800 ± 98

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 7.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	3.51	1260.0	24800
5	5.16	1100.0	21800
6	7.30	973.0	18100
7	9.65	866.0	15500
8	9.60	819.0	16300
10	12.64	640.0	14700
11	13.79	610.0	13800
12	16.67	504.0	12400
13	19.07	436.0	11400
14	21.09	415.0	10500
17	24.21	349.0	9580
18	24.63	342.0	9460
19	28.58	300.0	8390
20	29.78	294.0	8090
21	32.00	276.0	7620
23	35.22	238.0	7090
24	37.87	214.0	6700
25	39.74	197.0	6450
26	42.13	187.0	6120
27	63.98	121.0	4200

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	1580.0
	15	1910.0
	30	1780.0
Equilibrated Blanks		
	3	1810.0
	9	1840.0
	16	1820.0
	22	1830.0
	28	1790.0
	29	1890.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10 ± 1 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc., ug/L:** 538.0 ± 14.4

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 6.5

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	0.83	359.0	34540
4	2.07	166.0	28750
5	2.69	112.0	25330
6	3.55	71.2	31030
8	5.50	28.1	14800
9	6.77	18.5	12300
10	7.41	17.9	11200
11	8.00	13.7	10500
13	9.90	6.5	8590
14	10.44	10.0	8090
15	11.69	6.1	7280
16	13.90	—*	—
18	15.71	5.6	5420
19	17.75	—*	—
20	20.94	—*	—
22	23.66	—*	—
23	26.26	—*	—
24	24.52	—*	—
27	31.05	—*	—

Immediately Extracted Blanks:	I.D.	C_o, ug/L
Equilibrated Blanks	1	556.0
	2	558.0
	7	521.0
	12	529.0
	17	518.0
	21	541.0
	25	556.0
	28	536.0
	29	534.0

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*Concentration too low for accurate measurement.

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: $1.0 \times 10^{-3}M\ KH_2PO_4$ **Temperature, °C:** 10±1 **pH:** 6.0

Chemical: Tetrachloroethene **Initial Conc., ug/L:** 2770 ± 55

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 6

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	0.96	1169.3	266800
5	2.18	487.9	167500
6	1.84	531.8	194700
7	3.01	310.3	130800
8	2.02	442.1	184400
10	3.52	216.5	116100
11	4.77	116.4	89020
12	4.10	153.2	102100
13	5.78	69.4	74770
14	6.60	52.7	65890
17	7.38	35.9	59280
18	8.43	30.5	52000
19	9.44	27.8	46480
20	9.95	20.8	44200
21	11.42	15.6	38600
23	13.82	16.6	31890
24	15.72	90.1	--
25	17.87	8.5	24730
26	19.94	4.9	22190
27	23.06	3.5	19200

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	2756.2
	15	2673.9
	30	2769.9
Equilibrated Blanks	2	2767.4
	3	2744.5
	9	2887.5
	16	2772.1
	22	2748.1
	28	2765.1
	29	2819.5

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10 ± 1 **pH:** 6.0

Chemical: Bromoform **Initial Conc., ug/L:** 2950 ± 30

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 10.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	1.27	1970.0	123200
5	1.62	1720.0	121300
6	2.36	1320.0	110100
7	3.65	949.0	87690
8	3.04	1160.0	94400
10	3.94	917.0	82540
11	5.06	702.0	71080
12	5.74	565.0	66480
13	6.00	575.0	63320
14	6.69	488.0	58870
17	8.41	368.0	49120
18	9.38	315.0	44940
19	9.99	285.0	42670
20	13.78	166.0	32320
21	11.34	238.0	38250
23	14.28	157.0	31300
24	19.17	92.1	23850
25	22.34	79.3	20560
26	28.42	48.1	16340
27	33.56	38.3	13880

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	2983.0
	15	2948.0
	30	2966.0
Equilibrated Blanks		
	2	3015.0
	3	2928.0
	9	2935.0
	16	2929.0
	22	2934.0
	28	2930.0
	29	2929.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: $1.0x10^{-3}$M KH_2PO_4 **Temperature, °C:** 10 ± 1 **pH:** 6.0

Chemical: Chloroform **Initial Conc., ug/L:** 1417 ± 18

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 7.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	3.16	1180.0	11850
5	5.88	1050.0	9920
6	11.20	725.0	9890
7	17.88	478.0	8400
8	23.25	357.0	7300
10	29.48	308.0	6020
11	40.93	203.0	4750
12	47.63	156.0	4240
13	57.93	116.0	3600
14	70.79	81.6	3020
17	88.21	61.1	2460
18	105.88	94.1	2000
19	130.49	25.6	1710
20	158.68	23.1	1410
21	185.94	15.3	1210
23	221.80	11.4	1010
24	260.93	7.92	865
25	314.86	2.5	718
26	360.70	0.0	---
27	528.20	0.0	---

Immediately Extracted Blanks:	I.D.	C_o, ug/L
	1	1440.0
	16	1390.0
	30	1410.0
Equilibrated Blanks		
	2	1410.0
	3	1420.0
	9	1420.0
	15	1400.0
	22	1410.0
	28	1410.0
	29	1410.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature,°C:** 10 ± 1 **pH:** 6.0

Chemical: 1,2-Dibromoethane **Initial Conc.,ug/L:** 2431 ± 82

Water Matrix: Milli-Q Water **Equilibrium Time, days:** 7.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	1.06	2070.0	54690
5	1.78	1750.0	61340
6	3.82	1200.0	54300
7	5.00	891.0	49260
8	5.67	786.0	46400
10	6.80	663.0	41590
11	7.52	621.0	38490
12	9.00	---	---
13	10.59	373.0	31080
14	12.36	282.0	27810
17	14.50	195.0	24660
18	15.02	202.0	23740
19	17.52	180.0	20560
20	19.38	133.0	18970
21	22.63	102.0	16470
23	24.94	85.3	15050
24	28.00	66.5	13510
25	32.34	54.8	11750
26	36.38	39.0	10520
27	40.89	32.0	9390

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	2330.0
	15	2380.0
	30	2350.0
Equilibrated Blanks		
	2	2500.0
	9	2480.0
	22	2550.0
	29	2430.0
	16	---
	28	---

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: $1.0\text{x}10^{-3}$M KH_2PO_4 **Temperature,°C:** 10 ± 1 **pH:** 6.2

Chemical: Chlorodibromomethane **Initial Conc.,ug/L:** 2535 ± 109

Water Matrix: Milli-Water **Equilibrium Time, days:** 7.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	1.44	1830.0	78500
5	2.10	1820.0	54670
6	2.80	1670.0	49600
7	3.74	1300.0	52850
8	4.77	1090.0	48300
10	5.90	924.0	43690
11	6.79	894.0	38680
12	7.41	751.0	38530
13	9.38	537.0	34090
14	9.98	554.0	31770
17	10.67	470.0	30970
18	12.16	378.0	28380
19	14.95	277.0	24160
20	16.91	222.0	21890
21	18.83	203.0	19820
23	21.83	157.0	17430
24	22.52	160.0	16880
25	25.01	133.0	15370
26	27.16	104.0	14330
27	31.76	91.9	12310

Immediately Extracted Blanks:	**I.D.**	**C_o, ug/L**
	1	3630.0
	30	2560.0
Equilibrated Blanks	2	2380.0
	3	2440.0
	9	2370.0
	16	2630.0
	22	2630.0
	28	2610.0
	29	2590.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature,°C:** 13.8 ± 1 **pH:** 7.5 - 8

Chemical: DCE **Initial Conc., ug/L:** 7795 ± 0

Water Matrix: Milli-Q **Equilibrium Time, days:** 28

Sample #	Dosage, mg.	Volume, ml	C_e, umol/L	q_e, umol/g
1	12.7	158.3	55.5	310 *
2	16.09	159.6	42.6	375
3	21.64	156.7	43.2	269 *
4	27.88	156.7	27.9	295
5	31.10	158.4	24.5	284
6	14.92	42.1		
7	30.58	41.7		
8	48.21	42.3		
9	98.16	41.5		
10	138.48	41.4	.298	23.9
11	238.67	42.1	.117	14.2
12	344.58	41.2		

Immediately Extracted Blanks:	I.D.	C_o, ug/L
Equilibrated Blanks		
	B1	
	2	
	3	
	4	
	5	7795

---

* neglected in plot

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature,°C:** 13.8 ± 1 **pH:** 7.5 - 8

Chemical: TCE **Initial Conc., ug/L:** 9162 ± 34

Water Matrix: Milli-Q **Equilibrium Time, days:** 31

Sample #	Dosage, mg.	Volume, ml	C_e, umol/L	q_e, umol/g
1	6.81	157.6		
2	9.89	158.0	23.6	737
3	15.10	158.1		
4	22.11	157.9	6.67	450
5	33.05	158.1	3.26	318
6	38.40	157.8		
7	64.79	157.7		
8	90.82	157.9	0.322	121
9	30.20	43.0		
10	35.43	43.4	0.169	85.2
11	39.31	42.8	0.114	75.8
12	46.81	42.8		
13	12.59	158.1		
14	18.53	157.9		

Immediately Extracted Blanks: I.D. C_o, ug/L

Equilibrated Blanks

	I.D.	C_o, ug/L
	B1	9186
	2	
	3	
	4	
	5	
	6	
	7	9138

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200 x 400 mesh

Buffer: none **Temperature,°C:** 13.8 ± 1 **pH:** 7.5 - 8

Chemical: PCE **Initial Conc.,ug/L:** 10598 ± 0

Water Matrix: Milli-Q **Equilibrium Time, days:** 33

Sample #	Dosage, mg.	Volume, ml	C_e, umol/L	q_e, umol/g
1	1.95	158.0		
2	2.49	157.6	47.2	1057*
3	3.99	157.7		
4	6.11	157.9	15.7	1246
5	10.00	158.0		
6	20.24	158.1	1.27	489
7	27.78	157.3		
8	33.54	157.6	0.396	298
9	39.85	158.0		
10	45.13	158.0		
11	40.12	157.9	0.225	250
12	47.24	158.0	0.161	213
13	50.03	157.7		
14	3.00	157.9		
15	4.46	158.0		

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
Equilibrated Blanks		
	B1	
	2	
	3	
	4	10598

---

*neglected in plot

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature, °C:** 13.8 ± 1 **pH:** 7.5 - 8

Chemical: Toluene **Initial Conc., ug/L:** 7389 ± 638

Water Matrix: Milli-Q **Equilibrium Time, days:** 25

Sample #	Dosage, mg.	Volume,ml	C_e, umol/L	q_e, umol/g
1	Broken			
2	4.51	158.0	37.5	1500
3	6.33	157.9	24.0	1406
4	8.49	157.7	15.8	1198
5	10.28	158.0	12.08	1049
6	15.22	158.6	4.68	788
7	23.19	158.1	1.38	538
8	Broken			
9	39.78	158.6	0.300	319
10	45.47	158.0	0.187	278
11	53.54	157.7	0.122	236
12	69.59	158.4	0.0562	183

Immediately Extracted Blanks:	**I.D.**	**C_o, g/L**
Equilibrated Blanks		
	B2	8077
	3	7273
	4	6817

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature,°C:** 13.8 ± 1 **pH:** 7.5 - 8

Chemical: Ethyl Benzene **Initial Conc., ug/L:** 7485 ± 0

Water Matrix: Milli-Q **Equilibrium Time, days:** 21

Sample #	Dosage, mg.	Volume, ml	C_e, umol/L	q_e, umol/g
1	3.80	157.7	26.6	1826
2	5.15	157.9	12.4	1784*
3	6.90	157.6	8.4	1421
4	8.88	158.0	6.26	1144
5	10.56	157.3	2.46	1015
6	15.61	157.7	1.7	696
7	20.65	159.1	0.7	538
8	25.18	158.1	0.188	442
9	32.02	157.9	0.0901	368
10	40.91	157.8	0.0417	272

Immediately Extracted Blanks:	**I.D.**	**C_o, ug/L**
Equilibrated Blanks		
	B1	7485
	2	
	3	
	4	

---

* Neglected in plot

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature,°C:** 13.8±1 **pH:** 7.5 - 8

Chemical: M-Xylene **Initial Conc., ug/L:** 10778 ± 587

Water Matrix: Milli-Q **Equilibrium Time, days:** 21

Sample #	Dosage, mg.	Volume, ml	C_e, umol/L	q_e, umol/g
3	4.11	157.8	35.7	2412
4	4.45	158.0	28.7	2481
5	6.12	158.1	16.9	2110
6	10.09	157.6		
7	15.18	158.1		
8	19.11	157.8	0.363	811
9	25.91	157.3	broken	—
10	0.49	245.7		
11	0.80	245.0		
12	1.47	250.7		

Immediately Extracted Blanks:	I.D.	C_o, ug/L
Equilibrated Blanks		
	B1	10536
	B2	
	B3	10350
	B4	11447

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature,°C:** 13.8±1 **pH:** 7.5 - 8

Chemical: O-Xylene **Initial Conc., ug/L:** 7572 ± 404

Water Matrix: Milli-Q **Equilibrium Time, days:** 26

Sample #	Dosage, mg.	Volume, ml	C_e,umol/L	q_e,umol/g
4	2.08	158.0	41.3	2286
5	3.15	157.6	33.3	1908*
6	4.58	157.3		
7	6.18	157.8	8.54	1605
8	9.95	158.0	2.03	1101
9	15.37	157.9	0.497	728
10	31.98	157.6	ND	--
11	28.92	157.9	broken	--
12	38.83	157.3		

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
Equilibrated Blanks		
	B1	7908
	B2	7124
	B3	
	B4	7684

---

*neglected in plot

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** <200 Mesh

Buffer: 1x10^{-3}M, Phosphate **Temperature,°C:** 20-22 **pH:** 6.0

Chemical: Chloroform **Initial Conc.,ug/L:** 1430 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 2

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
1		1324	9604
2		1202	9484
3		1179	8132
4		1147	9166
5		1123	8280
6		1104	8939
7		1027	8145
8		978.0	7667
9		997.1	7000
10		1004.	5829
11		8810	7412
12		827.1	6509
13		813.0	6059
14		760.0	5476
15		648.0	5065
16		557.0	4710
17		544.0	4690
18		468.0	4374
19		502.0	4291
20		432.1	4020
21		451.0	3996
22		408.0	3688
23		375.0	3432
24		310.0	3023
25		262.0	2705
26		214.5	2355
27		175.0	2032
28		159.0	1700
29		125.9	1624
30		97.06	1270
31		81.06	1092
32		74.02	976.5
33		63.99	884.6
34		53.96	810.6
35		61.96	885.8
36		53.00	811.8
37		48.95	746.1
38		39.99	643.5
39		34.50	588.5

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol., ml:** **Carbon Size:** <200 Mesh

Buffer: $1\text{x}10^{-3}$M, Phosphate **Temperature, °C:** 20-22 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc., ug/L:** 983 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 2

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
1		527.8	23921
2		400.4	21006
3		214.0	15650
4		73.5	9473
5		36.8	6839
6		18.4	4938
7		6.04	2926
8		3.15	2156

Immediately Extracted Blanks: **I.D.** **C_o, ug/L**

Equilibrated Blanks

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** <200 Mesh

Buffer: 1x10^{-3}M, Phosphate **Temperature,°C:** 20-22 **pH:** 6.0

Chemical: Bromoform **Initial Conc.,ug/L:** 7050 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 2

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
1		3870	131700
2		2548	90990
3		2009	81590
4		1759	69560
5		1309	60280
6		995.8	49460
7		745.6	41270
8		545.9	35080
9		449.9	30530
10		348.8	27090
11		333.6	24140
12		273.0	21930
13		160.0	15970
14		84.92	11290
15		69.00	8687
16		56.11	6695
17		36.90	5702
18		25.00	4547
19		23.00	3789
20		20.00	3248
21		11.80	1839

Immediately Extracted Blanks: I.D. C_o, ug/L

Equilibrated Blanks

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 40x60

Buffer: $1x10^{-3}$M Phosphate **Temperature,°C:** 20-22 **pH:** 6.0

Chemical: Chloroform **Initial Conc.,ug/L:** 6880 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 6.4

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
1		5872	24200
2		5731	20100
3		4645	18790
4		3846	16210
5		3142	15020
6		2737	13190
7		1495	8673
8		626.0	5040
9		394.0	3587
10		202.0	2149
11		129.0	1958
12		39.00	1571

Immediately Extracted Blanks: I.D. C_o, ug/L

Equilibrated Blanks

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 40x60

Buffer: 1x10^{-3}M Phosphate **Temperature, °C:** 20-22 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc., ug/L:** 6365 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 6.4

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
1		3530	76581
2		1593	51558
3		949.4	42604
4		597.6	31575
5		314.8	23908
6		195.9	19260
7		90.94	13378
8		53.97	10125
9		31.98	7893
10		16.99	5143
11		12.59	4100
12		9.939	3410
13		0.550	2248

Immediately Extracted Blanks: **I.D.** **C_o, ug/L**

Equilibrated Blanks

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** - **Carbon Size:** 40x60

Buffer: 1x10^{-3}M, Phosphate **Temperature,°C:** 20-22 **pH:** 6.0

Chemical: Bromoform **Initial Conc.,ug/L:** 7557 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 6.4

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
1		3698	118900
2		2234	88460
3		857.1	49130
4		549.2	37200
5		348.0	27900
6		264.1	23610
7		151.0	16310
8		88.01	12060
9		61.01	9195
10		23.00	5722
11		16.30	4855
12		4.373	3554

Immediately Extracted Blanks: **I.D.** **C_o, ug/L**

Equilibrated Blanks

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** 160 **Carbon Size:** 60x80

Buffer: - **Temperature, °C:** 13.8 **pH:** 7.5

Chemical: TCE **Initial Conc.,umol/L:** 24 ±

Water Matrix: Milli-Q **Equilibrium Time, days:** 14

Sample #	Dosage, mg.	C_e, umol/L	q_e, umol/g
1	1.28	1.933	274.658
2	1.61	4.612	361.682
3	3.25	9.917	477.780
4	4.24	10.610	510.165
5	4.28	10.389	513.125
6	8.63	21.250	699.176

Immediately Extracted Blanks: **I.D.** **C_o, ug/L**

Equilibrated Blanks

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature,°C:** 10 ± 1 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc.,ug/L:** 682 ± 22

Water Matrix: Wausau Water (10/25/83) **Equilibrium Time, days:** 3
Spiked TCE

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4W2	1.09	555.5	18580
5W2	1.83	473.7	18220
6W2	2.51	410.1	17340
8W2	3.15	362.9	16210
9W2	4.37	254.5	15660
10W2	3.59	323.5	15980
11W2	4.94	237.4	14400
13W2	6.26	141.9	13810
14W2	7.60	110.7	12030
15W2	8.68	74.3	11200
16W2	10.08	55.9	9940
18W2	11.71	37.8	8800
19W2	13.43	27.3	7800
20W2	14.82	21.7	7130
21W2	16.18	19.1	6560
23W2	15.60	15.2	6840
24W2	18.27	14.1	5850
25W2	20.32	10.2	5290
27W2	25.11	5.5	4310
28W2	31.05	3.2	3500

	I.D.	C_o, ug/L
Immediately Extracted Blanks:	1W2	678.0
	12W2A	687.3
	29W2	683.3
Equilibrated Blanks	2W2	720.4
	7W2	687.2
	12W2B	682.8
	17W2	632.5
	22W2	702.9
	26W2	684.3
	30W2	665.5

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.2

Chemical: Cis-Dichloroethene **Initial Conc., ug/L:** 1240 ± 84

Water Matrix: Wausau Water (2/20/84) **Equilibrium Time, days:** 6.0
Spiked DCE

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	2.25	1310.0	--
4	3.26	1180.0	2940
5	4.57	950.0	10200
6	5.88	1250.0	--
7	7.98	1040.0	4010
9	9.95	921.0	5130
10	12.14	740.0	6610
11	13.91	655.0	6470
12	15.20	665.0	6080
14	17.41	585.0	6040
15	20.03	504.0	5900
16	23.32	414.0	5680
17	25.21	389.0	5410
19	27.50	339.0	5250
20	32.87	256.0	4800
21	35.72	222.0	4570
22	40.01	183.0	4230
23	47.33		

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	1250.0
	25	1260.0
Equilibrated Blanks	2	1910.0
	8	1170.0
	13	1580.0
	18	1160.0
	24	1370.0

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature,°C:** 10±1 **pH:** 6.2

Chemical: Trichloroethene **Initial Conc.,ug/L:** 1020 ± 7

Water Matrix: Wausau Water (2/20/84) **Equilibrium Time, days:** 6.0
Spiked TCE

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	2.93	668.0	18900
4	4.11		
5	5.47	381.0	18500
6	6.55		
7	7.65	226.0	16500
9	8.63	170.0	15700
10	10.18	127.0	14000
11	12.51	75.9	12000
12	13.50	61.0	11300
14	14.94	47.2	10400
15	16.44	37.7	9510
16	17.05	31.8	9230
17	19.26	24.7	8230
19	21.54	16.3	7420
20	23.32	11.1	6890
21	25.11	8.7	6410
22	27.61	5.8	5850
23	29.00	5.3	5570

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	1010.0
	25	1010.0
Equilibrated Blanks	2	1020.0
	8	1010.0
	12	1010.0
	18	1020.0
	25	1020.0

ISOTHERM DATA SHEET

Carbon Type: WV-G **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0x10^{-3}M KH_2PO_4 **Temperature, °C:** 10 ± 1 **pH:** 6.2

Chemical: Tetrachloroethene **Initial Conc., ug/L:** 1790 ± 10

Water Matrix: Wausau Water (2/20/84)
Spiked PCE **Equilibrium Time, days:** 6.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	1.30	1440.0	42700
4	1.90	1320.0	39700
5	1.52	1420.0	38600
6	2.19	1170.0	44800
7	2.41	1180.0	40100
9	2.87	1120.0	37300
10	3.42	991.0	37200
11	3.58	948.0	37500
12	4.13	757.0	39900
14	4.63	804.0	34000
15	5.04	524.0	40100
16	5.87	463.0	36100
17	6.34	356.0	36100
19	7.04	337.0	33000
20	6.56	342.0	35200
21	8.46	176.0	30500
22	9.79	105.0	27500
23	10.78	45.0	25900

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	1	1800.0
	25	1790.0
Equilibrated Blanks	2	1770.0
	8	1790.0
	13	1791.0
	18	1780.0
	24	1680.0

ISOTHERM DATA SHEET

Carbon Type: WV-G **Water Matrix:** Wausau Water (Well #4) with spiked TCE

Carbon Size: 200x400 mesh **Buffer:** No Buffer **Sampling Date:** 10/12/84

Temperature: 12±1°C **Equilibrium Time:** 7 days **pH:** 6.8 before and after equilibration

Sample #	Dosage (mg)	Cis-1,2-Dichloroethene		Trichloroethene		Tetrachloroethene		Toluene	Ethyl Benzene	m-Xylene	o,p-Xylene	Bottle Volume (ml)
		C_e (ug/1)	q_e (ug/g)	C_e (ug/1)	q_e (ug/g)	C_e (ug/1)	q_e (ug/g)	C_e (ug/1)	C_e (ug/1)	C_e (ug/1)	C_e (ug/1)	
Immediate Blank⁺	10/8/84	76.9		66.1		58.3		35.4	4.9	6.5	9.8	
	10/15/84	71.2		69.7		58.7		40.4	5.3	6.9	10.5	
Equilibrated Blank	—	50.5		517		30		ND	ND	ND	ND	
1	2.88	49.0	1390	175	19000	8.0	2800	ND	ND	ND	ND	160
2	4.46	36.0	1360	98.0	15000	4.0	2000	ND	ND	ND	ND	160
3	7.45	29.5	957	43.5	10200	4.0	1200	ND	2.5	ND	ND	160
4	12.77	15.1	739	12.9	6320	0.8	720	0.7	ND	ND	ND	160
5	16.62	56.3	171	53.0	4470	34.3	240	ND	ND	ND	ND	160
6	19.65	8.5	534	5.1	4170	0.7	470	ND	ND	ND	ND	160
7	27.25	6.2	398	3.4	3020	0.7	330	ND	ND	ND	ND	160

ND-Non Detectable

⁺Immediate blanks of 10/8 and 10/15 were averaged for initial concentration

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.0

Chemical: Trichloroethene **Initial Conc., ug/L:** 604.4 ± 29.9

Water Matrix: Wausau Water (10/25/83)
Spiked TCE
Equilibrium Time, days: 5.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3W3	2.23	282.7	23100
TCE5W3	3.43	147.6	21310
TCE9W3	5.14	70.6	16620
TCE8W3	2.21	280.7	23440
TCE10W3	4.40	121.4	17560
TCE18W3	11.36	13.7	8320
TCE28W3	31.07	0.5*	--
TCE23W3	20.61	3.0*	--
TCE11W3	4.88	56.3	17970
TCE15W3	8.59	17.5	10930
TCE4W3	1.72	319.5	26500
TCE24W3	22.23	1.6*	--
TCE13W3	7.71	41.0	11690
TCE25W3	27.59	0.1*	--
TCE16W3	10.00	13.5	9450
TCE27W3	25.25	0.9*	--
TCE20W3	15.85	5.0	6050
TCE21W3	18.86	3.4*	--
TCE14W3	6.22	50.2	14260
TCE6W3	3.32	153.0	21750
TCE19W3	13.85	10.3	6860

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
Equilibrated Blanks	TCE12W3	662.8
	TCE29W3	599.4
	TCE17W3	600.8
	TCE7W3	574.7
	TCE2W3	580.3
	TCE22W3	591.5
	TCE26W3	621.5

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*Data points not used due to concentrations too low for accurate measurement.

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.2

Chemical: Cis-Dichloroethene **Initial Conc., ug/L:** 1170 ± 27

Water Matrix: Wausau Water (2/20/84) Spiked DCE **Equilibrium Time, days:** 6.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	2.11	1110.0	4550
4	2.76	1220.0	--
5	4.24	1200.0	--
6	6.11	1110.0	1570
7	8.17	996.0	3410
9	9.98	719.0	7230
10	11.83	703.0	6320
11	14.05		
12	15.61	592.0	5930
14	17.45	515.0	6010
15	19.99	440.0	5840
16	24.57	354.0	5320
17	25.83	343.0	5120
19	28.00	293.0	5010
20	32.29	239.0	4620
21	36.02	200.0	4310
22	40.20	165.0	4000
23	47.22	143.0	3480

Immediately Extracted Blanks:	I.D.	C_o, ug/L
	1	1140.0
	25	1460.0
Equilibrated Blanks	2	1220.0
	8	1160.0
	12	1170.0
	18	1160.0
	24	1180.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: $1.0x10^{-3}M\ KH_2PO_4$ **Temperature, °C:** 10±1 **pH:** 6.2

Chemical: Trichloroethene **Initial Conc., ug/L:** 1001 ± 9

Water Matrix: Wausau Water (2/20/84) **Equilibrium Time, days:** 6.0
Spiked TCE

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	1.85	720.0	24400
4	2.48	629.0	24100
5	3.08	561.0	22900
6	4.00	439.0	22500
7	4.89	322.0	22300
9	5.50	288.0	20800
10	7.11	186.0	18400
11	8.12		
12	8.80	98.6	16400
14	9.70	89.9	15100
15	10.75	73.4	13800
16	10.90	72.2	13600
17	12.60	47.9	12100
19	14.26	32.6	10900
20	15.32	25.0	10200
21	16.61	19.3	9470
22	17.46	20.1	9000
23	19.94	13.3	7940

Immediately Extracted Blanks:	I.D.	C_o, ug/L
	1	996.0
	25	1000.0
Equilibrated Blanks	2	1000.0
	8	1020.0
	12	996.0
	18	996.0
	24	1000.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: $1.0\text{x}10^{-3}$M KH_2PO_4 **Temperature, °C:** 10±1 **pH:** 6.2

Chemical: Trichloroethene **Initial Conc., ug/L:** 896.0 ± 21.8

Water Matrix: Wausau Water (2/20/84) (presaturated) **Equilibrium Time, days:** 4.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	1.71	557.0	31700
4	2.32	457.0	30300
5	3.07	374.0	27200
6	4.14	270.0	24200
7	5.30	182.0	21500
9	6.02	135.0	20200
10	7.47	102.0	17000
11	8.07	84.9	16100
12	8.91	79.1	14700
14	9.47	61.6	14100
15	10.29	54.0	13100
16	11.18	43.0	12200
17	12.31	30.9	11200
19	14.06	23.4	9930
20	15.33	19.2	9150
21	16.28	18.2	8630
22	18.08	14.7	7800
23	19.16	9.4	7403

Immediately Extracted Blanks:	I.D.	C_o, ug/L
	1	883.0
	25	892.0
Equilibrated Blanks	2	919.0
	8	866.0
	13	878.0
	18	907.0
	24	925.0

Note: Presaturation of the carbon was completed with 100 ml of purged Wausau water for 20 min using helium at 6 ml per seconds. After 4 days of equilibration, 60 ml of spiked Wausau water was added and equilibrated for 4 days.

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0x10^{-3}M KH_2PO_4 **Temperature,°C:** 10±1 **pH:** 6.5

Chemical: Trichloroethene **Initial Conc.,ug/L:** 1030 ± 46

Water Matrix: Wausau Water (2/20/84) (diluted) **Equilibrium Time, days:** 6.0

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	1.80	557.0	42200
4	2.52	480.0	34900
5	3.06	366.0	34800
6	3.74	282.0	32100
7	4.76	195.0	28100
9	5.65	167.0	24500
10	6.76	98.7	22100
11	8.17	66.0	18900
12	8.95	61.0	17300
14	9.10	70.2	16900
15	10.41	36.5	15300
16	11.77	33.7	13600
17	12.34	25.7	13000
19	14.09		
20	15.27	13.7	10700
21	16.33	10.9	9990
22	18.00	10.0	9080
23	19.34	9.4	8450

Immediately Extracted Blanks:	I.D.	C_o, ug/L
	1	966.0
	25	1070.0
Equilibrated Blanks	2	988.0
	8	1010.0
	13	1090.0
	18	1060.0
	24	1030.0

Note: Dilution was 50 ml Milli-Q + 110 ml spiked Wausau water.

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0x10^{-3}M KH_2PO_4 **Temperature, °C:** 10 ± 1 **pH:** 6.3

Chemical: Tetrachloroethylene **Initial Conc.,ug/L:** 1731 ± 100

Water Matrix: Wausau Water (2/20/84) Spiked PCE **Equilibrium Time, days:** 7

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	0.93	990.3	127400
4	1.27	728.2	126300
5	--	--	--
6	2.16	307.4	105500
7	2.04	246.0	116500
9	2.76	188.5	89400
10	2.29	209.6	106300
11	3.27	117.5	78950
12	3.59	94.8	72920
14	3.81	103.8	68330
15	4.36	61.5	61270
16	4.67	39.6	57950
17	5.27	41.0	51310
19	5.72	30.6	47560
20	6.64	14.4	41360
21	8.02	10.7	34320
22	7.75	11.2	35510
23	--		

	I.D.	C_o, ug/L
Immediately Extracted Blanks:		
	2	1865.4
	25	1837.1
Equilibrated Blanks		
	1	1674.8
	8	1753.5
	13	1735.3
	18	1574.5
	24	1676.3

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol,ml** = 160 **Carbon Size:** 200x400 mesh

Buffer: 1.0×10^{-3}M KH_2PO_4 **Temperature, °C:** 10 ± 1 **pH:** 6.2

Chemical: Tetrachloroethene **Initial Conc., ug/L:** 1790 ± 26

Water Matrix: Wausau Water (2/20/84) **Equilibrium Time, days:** 6.0
Spiked PCE

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
3	1.19	1420.0	50000
4	1.32	1370.0	50900
5	3.25	1020.0	37900
6	1.68	1440.0	33400
7	2.00	1350.0	35400
9	2.31	1240.0	38100
10	2.51	1170.0	39900
11	3.14	1070.0	36700
12	3.77	889.0	38400
14	3.62	953.0	37100
15	4.23	789.0	38000
16	4.97	579.0	39100
17	5.24	608.0	36200
19	5.63	341.0	41300
20	6.83	204.0	37200
21	7.03	282.0	34400
22	7.62	247.0	32500
23	9.39	60.0	29500

Immediately Extracted Blanks:	**I.D.**	**C_o, ug/L**
	1	1800.0
	25	1846.0
Equilibrated Blanks	2	1794.0
	8	1783.0
	12	1784.0
	18	1760.0
	24	1784.0

ISOTHERM DATA SHEET

Carbon Type: F-400 **Water Matrix:** Wausau Water with spiked TCE

Carbon Size: 200x400 mesh **Buffer:** No Buffer **Sampling Date:** 10/12/84

Temperature: 12±1°C **Equilibrium Time:** 7 days **pH:** 6.8 before and after equilibration

Sample #	Dosage (mg)	Cis-1,2-Dichloroethene		Trichloroethene		Tetrachloroethene		Tolune	Ethyl Benzene	M-Xylene	O,P-Xylene	Bottle Volume (ml)
		C_e (ug/1)	q_e (ug/g)	C_e (ug/1)	q_e (ul/g)	C_e (ug/1)	q_e (ug/g)	C_e (ug/1)	C_e (ug/1)	C_e (ug/1)	C_e (ug/1)	
Immediate Blank$^+$	10/8/84	76.9		66.1		58.3		35.4	4.9	6.5	9.8	
	10/15/84	71.2		69.7		58.7		40.4	5.3	6.9	10.5	
Equilibrated Blank	—	50.7		520		30.1		ND	ND	ND	ND	160
1	2.19	42.0	2340	138	27900	8.0	3700	ND	ND	ND	ND	160
2	2.46	38.5	2310	168	22900	4.5	3500	ND	ND	ND	ND	160
3	4.71	33.5	1380	64.5	15500	4.0	1900	2.5	ND	ND	ND	160
4	8.35	18.1	1070	21.5	9550	0.9	1100	ND	ND	ND	ND	160
5	10.61	65.6	127	69.1	6800	20.3	580	ND	ND	ND	ND	160
6	14.05	10.4	725	8.0	5800	0.8	660	ND	ND	ND	1.8	160
7	17.21	9.4	600	8.6	4800	0.8	540	ND	0.4	1.4	1.7	160

ND-Non Detectable

$^+$Immediate blanks of 10/8 and 10/15 were averaged for initial concentration

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature, °C:** 12.0 ± 1C **pH:** 6.3 before and after equilibration

Chemical: TOX **Date:** 12/6/84 **Initial Conc., ug/L:** 130±14

Water Matrix: Raw Wausau Water **Equilibration times:** 6 days

Sample #	Dosage, mg.	TOX C_e, ug/L	q_e, ug/g	Bottle Volume ml
3	127	35	789	1.054
4	219	19	600	1.181
5	371	10	341	1.053
6	684	6	180	0 .995

Immediately Extracted Blanks:	I.D.	C_o, ug/L
Equilibrated Blanks		
	1	120
	7	140

ISOTHERM DATA SHEET

Carbon Type: F-400 **Water Matrix:** Raw Wausau Water

Carbon Size: 200x400 mesh **Buffer:** No Buffer **Sampling Date:** 4/8/85

Temperature: 13.8 ± 1°C **Equilibrium Time:** 7 days **pH:** 6.4 before and after equilibration

Sample #	Dosage (mg)	Cis-1,2-Dichloroethene C_e (ug/l)	Cis-1,2-Dichloroethene q_e (ug/g)	Trichloroethene C_e (ug/l)	Trichloroethene q_e (ug/g)	Tetrachloroethene C_e (ug/l)	Tetrachloroethene q_e (ug/g)	Bottle (ml)
Immediate Blank		55.5		22.8		25.7		
		53.6		28.4		24.3		
Equilibrated		57.1		23.7		25.2		
		58.5		25.4		28.5		
1	2.52	48.4	1535	16.2	1476	13.5	2400	498
2	3.16	50.1	964	14.3	1488	11.5	2184	502
3	2.57	48.6	1470	16.0	1489	13.6	2262	499
4	3.30	47.0	1386	12.1	1748	8.0	2607	499
5	1.75	48.0	1186	15.9	1126	13.4	1718	254
6	2.41	42.6	1404	7.8	1642	3.1	2291	249
7	3.08	40.1	1326	7.8	1310	4.5	1713	250
8	3.48	37.2	1192	6.6	1073	3.4	1373	250
9	4.13	35.5	1247	3.2	1235	1.0	1463	249
10	4.31	36.8	1152	6.4	1027	3.1	1317	256
11	7.20	22.2	1200	0.8	808	.3	881	254
12	10.00	15.8	1016	0.3	588	ND	—	252
13	14,83	9.1	791	ND	—	.2	—	249

Immediately extracted blanks (ug/L)

op-xyl	DCE	TCE	PCE	111-TCE	BENZENE	tol	EB	m-xyl
9.4	70.7	34.1	36.2	0.7	X	18.3	4.7	5.1

Vinyl Chloride

20.6

Equilibrated Blanks (ug/L)

VC	DCE	TCE	PCE	111-TCE	ben	tol	EB	M-xyl	op-xyl
4.4	55.5	22.8	25.7	0.3	X	0.4	X	2.1	5.1
4.7	57.1	23.7	25.2	0.5	X	0.3	X	1.9	4.8
8.0	58.5	25.4	25.8	0.6	X	X	0.8	2.1	5.7
13.0	64.8	28.4	26.9	0.6	X	6.9	3.1	3.0	7.1

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol., ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature, °C:** 13.8 ± 1 **pH:** 6.3 before and after equilibration

Chemical: TOX **Date:** 4/8/85 **Initial Conc., ug/L:** 118±8

Water Matrix: Raw Wausau Water **Equilibration times:** 8 days

Sample #	Dosage, mg.	TOX C_e, ug/L	TOX q_e, ug/g	Bottle Volume ml
1	--	--	--	--
2	6.13	85	5753	1058
3	11.38	85	3096	1057
4	24.00	65	2356	1060
5	48.13	50	1499	1056
6	86.75	30	1078	1059
7	--	--	--	--
8	134.1	22	760	1058
9	222.4	11	510	1056
10	380.5	7	292	997
11	693.1	2	178	1058

Immediately Extracted Blanks:	**I.D.**	**C_o, ug/L**
Equilibrated Blanks		
	1	125
	7	110
	12	120

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature, °C:** 13.8 ± 1 **pH:** 6.3 before and after equilibration

Chemical: TOX **Date:** 4/8/85 **Initial Conc., ug/L:** 118±8

Water Matrix: Diluted Raw Wausau Water **Equilibration times:** 8 days

Sample #	Dosage, mg.	TOX C_e, ug/L	q_e, ug/g	Bottle Volume L
14	5.46	50	2450	1.053
15	12.26	—	--	1.062
16	27.02	25	1670	1.061
17	32.65	30	1210	1.057
19	50.01	22	862	1.056
20	113.54	8	459	1.004
21	265.11	4	238	1.065
23	80.46	10	773	1.061

Immediately Extracted Blanks: I.D. C_o, ug/L

Equilibrated Blanks

Initial concentrations were found from the percentage diluted. See non-diluted isotherm for initial concentration.

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** **Carbon Size:** 200x400 mesh

Buffer: none **Temperature, °C:** 13.8 ± 1 **pH:** 6.3 before and after equilibration

Chemical: TOC **Date:** 5/2/85 **Initial Conc.,mg/L:** 8.08

Water Matrix: Wausau Water **Equilibration times:** 10 days

Sample Code	Dosage, g	Volume, ml	Ce, mg/L	q_e, mg/g
TOC1	0.65249	162	0.85	1.80
TOC2	0.60285	162	0.79	1.96
TOC3	0.55094	162	0.82	2.13
TOC4	0.49782	162	0.87	2.35
TOC5	0.47768	162	0.75	2.49
TOC6	0.44917	162	0.82	2.62
TOC7	0.42412	162	0.78	2.79
TOC8	0.39921	162	0.82	2.95
TOC9	0.37710	162	0.67	3.18
TOC10	0.35134	162	0.90	3.31
TOC11	0.32777	162	0.71	3.64
TOC12	0.30143	162	0.81	3.91
TOC13	0.27908	162	0.81	4.22
TOC14	0.25990	162	0.75	4.57
TOC15	0.10606	162	1.24	10.45
TOC16	0.19953	162	0.78	5.93
TOC17	0.18864	162	0.91	6.16
TOC18	0.16050	162	0.93	7.22
TOC19	0.22629	162	---	---
TOC20	0.10116	162	0.98	11.37
TOC21	0.05245	162	1.67	19.80
TOC22	0.07968	162	1.07	14.25
TOC23	0.03488	162	1.81	29.12
TOC24	0.01829	162	2.93	45.62
TOC25	0.01138	162	4.56	50.11

Immediately Extracted Blanks:	I.D.	C_o, mg/L
Equilibrated Blanks		8.08
		8.08 unfiltered 8.09 filtered

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** 160 **Carbon Size:** 200 x 400

Buffer: None **Temperature,°C:** 13.8 **pH:** 6.4

Chemical: TOC **Initial Conc.,mg/L:** 8.68 ± 0.58

Water Matrix: Wausau Water 3-30-86 **Equilibrium Time, days:** 10

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
4	298.8	1.16	4.03
5	197.8	0.74	6.39
7	100.8	1.20	11.87
8	74.8	1.36	15.67
9	50.8	1.69	22.00
11	25.1	3.04	35.92
12	25.5	4.16	28.36
13	20.0	4.56	32.96
15	15.2	5.16	37.28
16	9.73	6.68	32.89
17	4.97	7.44	39.92
19	1.90	7.92	64.00

Immediately Extracted Blanks:	I.D.	C_o, ug/L
Equilibrated Blanks		
	1	9.88
	2	9.40
	10	8.20
	14	8.76
	18	8.76
	22	8.16
	26	8.56
	30	8.68
	34	8.08
	35	8.32

ISOTHERM DATA SHEET

Carbon Type: F-400 **Bottle Vol.,ml:** - **Carbon Size:**

Buffer: - **Temperature,°C:** 13 ± 2 **pH:**

Chemical: TOX **Initial Conc.,ug/L:** -

Water Matrix: Wausau Water
From Pilot Plant 5-29-85 **Equilibrium Time, days:** -

Sample #	Dosage, mg.	C_e, ug/L	q_e, ug/g
D 8/9 A	-	105	15100
D 9/10 A	-	90	10900
D 10/11 A	-	90	7600
D 11/12 A	-	85	6600
D 12/13 A	-	80	1800
D 13/14 A	-	60	2300

APPENDIX V.   DETERMINATION OF SOLUBILITIES USING UNIFAC

```
C
C          THIS PROGRAM WILL CALCULATE THE SOLUBILITY OF COMPOUNDS
C      USING UNIFAC DERIVED ACTIVITY COEFICIENTS.  THE PROGRAM WILL
C      USE THESE ACTIVITY COEFICIENTS IN TWO DIFFERENT EQUATIONS
C      TO CALCULATE THE SOLUBILITY
C
C      PROGRAM WRITTEN BY:THOMAS FRANCIS PETER SPETH
C
C      PROGRAM LANGUAGE:  FORTRAN-77
C
C      VARIABLE DEFINITIONS:
C
C      A     = GROUP INTERACTION PARAMETER
C      AA    = GROUP INTERACTION PARAMETER
C      AC    = ln(ACT)
C      ACT   = ACTIVITY COEFFICIENT
C      AGAIN = TO DETERMINE WHETHER TO RUN THE PROGRAM OR NOT
C      CN    = COMPONENT NUMBER
C      GAC   = GROUP ACTIVITY COEFFICIENT FOR PURE SOLUTE
C      GACW  = GROUP ACTIVITY COEFFICIENT FOR PURE WATER
C      GSAF  = GROUP SURFACE AREA FRACTION FOR SOLUTE
C      GSAFW = GROUP SURFACE AREA FRACTION FOR SOLVENT
C      I     = COUNTER
C      J     = COUNTER
C      K     = COUNTER
C      L1    = UNIFAC PARAMETER
C      L2    = UNIFAC PARAMETER
C      LNYC  = COMBINATORIAL PORTION OF SOLUTE ACTIVITY COEFFICIENT
C      LNYR  = RESIDUAL PORTION OF ACTIVITY COEFFICIENT
C      MGN   = MAIN GROUP NUMBER
C      MMX   = ARRAY DESCRIBER
C      MMY   = ARRAY DESCRIBER
C      MW    = MOLECULAR WEIGHT
C      NAME  = NAME OF COMPOUND
C      NUM   = NUMBER OF DIFFERENT FUNCTIONAL GROUPS
C      Q     = VAN DER WAALS SURFACE AREA
C      Q1    = VAN DER WAALS SURFACE AREA FOR SOLUTE
C      Q2    = VAN DER WAALS SURFACE AREA FOR SOLVENT
C      QT    = SUMMATION OF Q*X
C      QQ    = VAN DER WAALS SURFACE AREA
C      R     = VAN DER WAALS GROUP VOLUME
C      R1    = VAN DER WAALS GROUP VOLUME FOR SOLUTE
C      R2    = VAN DER WAALS GROUP VOLUME FOR SOLVENTS
C      RR    = VAN DER WAALS GROUP VOLUME
C      SOL1  = SOLUBILITY USING FIRST CORRELATION - SEE BELOW
C      SOL2  = SOLUBILITY USING SECOND CORRELATION - SEE BELOW
C      SUM1  = SUMMATION TO CALCULATE GROUP ACTIVITY COEFFICIENT-SOLUTE
C      SUM2  = SUMMATION TO CALCULATE GROUP ACTIVITY COEFFICIENT-SOLUTE
C      SUM3  = SUMMATION TO CALCULATE GROUP ACTIVITY COEFFICIENT-SOLUTE
C      T     = TEMPERATURE OF DESIRED SOLUBILITY
C      VK    = NUMBER OF A SPECIFIC FUNCTIONAL GROUP ON THE COMPOUND
C      VKT   = SUMMATION OF VK
```

```
C     X     = GROUP FRACTION FOR SOLUTE
C     XW    = GROUP FRACTION FOR SOLVENT
C     YY    = UNIFAC PARAMETER
C
C
C     CORRELATION ONE:  SOL1=55.5/ACT
C
C     CORRELATION TWO:  ln (SOL2) = 1.2 + 0.782 * ln (1/ACT)
C
C
C     SAMPLE INPUT:  NONE, THE PROGRAM IS USER INTERACTIVE.  THE
C     ONLY INFORMATION REQIURED ARE:
C
C     NAME OF SOLUTE
C     MOLECULAR WEIGHT
C     NUMBER OF DIFFERENT FUNTIONAL GROUPS IN SOLUTE AND SOLVENT
C     MAIN GROUP NUMBER OF THE FUNCTIONAL GROUPS
C     COMPONENT NUMBER OF THE FUNCTIONAL GROUPS
C     NUMBER OF SPECIFIC FUNCTIONAL GROUPS ON COMPOUND
C     TEMPERATURE OF NEEDED SOLUBILITY (DEGREES CELSIUS)
C
C     EXPLAINATION OF DATA BASE:
C
C     MAIN GROUP    COMPONENT     FUNCTIONAL
C      NUMBER        NUMBER         GROUP
C
C        1             1             CH3
C        1             2             CH2
C        1             3             CH
C        1             4             C
C        2             5             CH2=CH
C        2             6             CH=CH
C        2             7             CH2=C
C        2             8             CH=C
C        2             9             C=C
C        3            10             ACH
C        3            11             AC
C        4            12             ACCH3
C        4            13             ACCH2
C        4            14             ACCH
C        5            15             OH
C        6            16             CH3OH
C        7            17             H2O
C        8            18             ACOH
C        9            19             CH3CO
C        9            20             CH2CO
C       10            21             CHO
C       11            22             CH3COO
C       11            23             CH2COO
C       12            24             HCOO
C       13            25             CH3O
C       13            26             CH2O
C       13            27             CH-O
C       13            28             FCH2O
C       14            29             CH3NH2
```

```
C        14          30          CH2NH2
C        14          31          CHNH2
C        15          32          CH3NH
C        15          33          CH2NH
C        15          34          CHNH
C        16          35          CH3N
C        16          36          CH2N
C        17          37          ACNH2
C        18          38          C5H5N
C        18          39          C5H4N
C        18          40          C5H3N
C        19          41          CH3CN
C        19          42          CH2CN
C        20          43          COOH
C        20          44          HCOOH
C        21          45          CH2Cl
C        21          46          CHCl
C        21          47          CCl
C        22          48          CH2Cl2
C        22          49          CHCl2
C        22          50          CCl2
C        23          51          CHCl3
C        23          52          CCl3
C        24          53          CCl4
C        25          54          ACCl
C        26          55          CH3NO2
C        26          56          CH2NO2
C        26          57          CHNO2
C        27          58          ACNO2
C        28          59          CS2
C        29          60          CH3SH
C        29          61          CH2SH
C        30          62          FURFURAL
C        31          63          (CH2OH)2
C        32          64          I
C        33          65          Br
C        34          66          CH=-C
C        34          67          C=-C
C        35          68          DIMETHYLSULFOXIDE
C        36          69          ACRYLONITRILE
C        37          70          Cl-(C=C)
C        38          71          ACF
C        39          72          DMF-1
C        39          73          DMF-2
C        40          74          CF3
C        40          75          CF2
C        40          76          CF
C
C
C     WHERE, ALL NUMBERS ARE SUBSCRIPTS, =- INDICATES TRIPLE BOND,
C
C     AC = AROMATIC RING CARBON         N  = NITROGEN
C     BR = BROMOFORM                    O  = OXYGEN
C     C  = CARBON                       S  = SULFER
C     Cl = CHLORINE
```

```
C     DOH= DIOL
C     F  = FLOURINE
C     H  = HYDROGEN
C
C
C     PROGRAM
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION RR(76),QQ(76),AA(40,40),MGN(20),VK(20),Q(20),X(20)
      DIMENSION YY(20,20),R(20),GSAF(20),GAC(20),GACW(20),A(20,20),T(50)
      DOUBLE PRECISION L1,L2,LNYC,LNYR,MW
      INTEGER CN(20)
      CHARACTER*20 NAME
      CHARACTER*3 AGAIN
      DATA (RR(I), I=1,76) / 0.9011D0,0.6744D0,0.4469D0,0.2195D0,
     $1.3454D0,1.1167D0,1.1173D0,0.8886D0,0.6605D0,0.5313D0,0.3652D0,
     $1.2663D0,1.0396D0,0.8121D0,1.0000D0,1.4311D0,0.9200D0,0.8952D0,
     $1.6724D0,1.4457D0,0.9980D0,1.9031D0,1.6764D0,1.2420D0,1.1450D0,
     $0.9183D0,0.6908D0,0.9183D0,1.5959D0,1.3692D0,1.1417D0,1.4337D0,
     $1.2070D0,0.9795D0,1.1865D0,0.9597D0,1.0600D0,2.9993D0,2.8832D0,
     $2.6670D0,1.8701D0,1.6434D0,1.3013D0,1.5280D0,1.4654D0,1.2380D0,
     $1.0060D0,2.2564D0,2.0606D0,1.8016D0,2.8700D0,2.6401D0,3.3900D0,
     $1.1562D0,2.0086D0,1.7818D0,1.5544D0,1.4199D0,2.0570D0,1.8770D0,
     $1.6510D0,3.1680D0,2.4088D0,1.2640D0,0.9492D0,1.2920D0,1.0613D0,
     $2.8266D0,2.3144D0,0.7910D0,0.6948D0,3.0856D0,2.6322D0,1.4060D0,
     $1.0105D0,0.6150D0 /
      DATA (QQ(I), I=1,76) / 0.848D0,0.540D0,0.228D0,0.000D0,1.176D0,
     $0.867D0,0.988D0,0.676D0,0.485D0,0.400D0,0.120D0,0.968D0,0.660D0,
     $0.348D0,1.200D0,1.432D0,1.400D0,0.680D0,1.488D0,1.180D0,0.948D0,
     $1.728D0,1.420D0,1.188D0,1.088D0,0.780D0,0.468D0,1.100D0,1.544D0,
     $1.236D0,0.924D0,1.244D0,0.936D0,0.624D0,0.940D0,0.632D0,0.816D0,
     $2.113D0,1.833D0,1.558D0,1.724D0,1.416D0,1.224D0,1.532D0,1.264D0,
     $0.952D0,0.724D0,1.988D0,1.684D0,1.448D0,2.410D0,2.184D0,2.910D0,
     $0.844D0,1.868D0,1.560D0,1.248D0,1.104D0,1.650D0,1.676D0,1.368D0,
     $2.484D0,2.248D0,0.992D0,0.832D0,1.088D0,0.784D0,2.472D0,2.052D0,
     $0.724D0,0.524D0,2.736D0,2.120D0,1.380D0,0.920D0,0.460D0 /
      DATA (AA(I,1), I=1,40) / 0.0D0,2520.0D0,-11.12D0,-69.7D0,156.4D0,
     $16.51D0,300.0D0,10000.0D0,26.76D0,505.7D0,114.8D0,90.49D0,83.36D0,
     $-30.48D0,65.33D0,-83.98D0,5339.0D0,-101.6D0,24.82D0,315.3D0,
     $91.46D0,34.01D0,36.7D0,-78.45D0,-141.3D0,-32.69D0,5541.0D0,
     $-52.65D0,-7.481D0,-25.31D0,140.0D0,128.0D0,-31.52D0,-72.88D0,
     $50.49D0,-165.9D0,41.9D0,-5.132D0,-31.95D0,147.3D0 /
      DATA (AA(I,2), I=1,40) / -200.0D0,0.0D0,-94.78D0,-269.7D0,
     $8694.0D0,-52.39D0,692.7D0,732.2D0,-82.92D0,1.0D0,362.4D0,91.65D0,
     $76.44D0,79.4D0,-41.32D0,-188.0D0,1.0D0,1.0D0,34.78D0,349.2D0,
     $-24.36D0,-52.71D0,-185.1D0,-293.7D0,-203.2D0,-49.92D0,1.0D0,
     $16.62D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0,-184.4D0,1.0D0,1.0D0,
     $-3.167D0,1.0D0,37.7D0,1.0D0 /
      DATA (AA(I,3), I=1,40) / 61.130D0,340.7D0,0.0D0,-146.8D0,89.6D0,
     $-50.0D0,362.3D0,270.2D0,140.1D0,1.0D0,85.84D0,1.0D0,52.13D0,
     $-44.85D0,-22.31D0,-223.9D0,650.4D0,31.87D0,-22.97D0,62.32D0,
     $4.68D0,121.3D0,288.5D0,-4.7D0,-237.7D0,10.38D0,1824.0D0,21.5D0,
     $28.41D0,157.3D0,221.4D0,58.68D0,155.6D0,1.0D0,-2.504D0,1.0D0,
     $-75.67D0,-237.2D0,-133.9D0,1.0D0 /
      DATA (AA(I,4), I=1,40) / 76.5D0,4102.0D0,167.0D0,0.0D0,25.82D0,
$-44.5D0,377.6D0,10000.0D0,365.8D0,1.0D0,-170.0D0,1.0D0,65.69D0,
$1.0D0,223.0D0,109.9D0,979.8D0,49.8D0,-138.4D0,268.2D0,122.9D0,
$1.0D0,33.61D0,134.7D0,375.5D0,-97.05D0,-127.8D0,40.68D0,1.0D0,
$404.3D0,150.6D0,1.0D0,291.1D0,1.0D0,-143.2D0,1.0D0,1.0D0,-157.3D0,
$-240.2D0,1.0D0 /
 DATA (AA(I,5), I=1,40) / 986.5D0,693.9D0,636.1D0,803.2D0,0.0D0,
$249.1D0,-229.1D0,-274.5D0,164.5D0,-404.8D0,245.4D0,191.2D0,
$237.7D0,-164.0D0,-150.0D0,28.6D0,529.0D0,-132.3D0,185.4D0,
$-151.0D0,562.2D0,747.7D0,742.1D0,856.3D0,246.9D0,341.7D0,561.6D0,
$823.5D0,461.6D0,521.6D0,267.6D0,501.3D0,721.9D0,1.0D0,-25.87D0,
$1.0D0,640.9D0,649.7D0,64.16D0,1.0D0 /
 DATA (AA(I,6), I=1,40) / 697.2D0,1509.0D0,637.35D0,603.25D0,
$-137.1D0,0.0D0,289.6D0,-111.6D0,108.7D0,-340.2D0,249.63D0,155.7D0,
$339.72D0,-481.7D0,-500.4D0,-406.8D0,5.182D0,-378.2D0,157.8D0,
$1020.0D0,529.0D0,669.9D0,649.1D0,860.1D0,661.6D0,252.6D0,1.0D0,
$914.2D0,382.8D0,5*1.0D0,695.0D0,1.0D0,726.7D0,645.9D0,172.2D0,
$1.0D0 /
 DATA (AA(I,7), I=1,40) / 1318.0D0,634.2D0,903.8D0,5965.0D0,
$353.5D0,-181.0D0,0.0D0,531.3D0,472.5D0,232.7D0,10000.0D0,1.0D0,
$-314.7D0,-330.4D0,-448.2D0,-598.8D0,-339.5D0,-332.9D0,242.8D0,
$-56.17D0,698.2D0,708.7D0,826.76D0,1201.0D0,920.4D0,417.9D0,
$360.7D0,1081.0D0,1.0D0,23.48D0,0.0D0,1.0D0,285.0D0,1.0D0,
$-240.0D0,386.6D0,1.0D0,1.0D0,-287.1D0,1.0D0 /
 DATA (AA(I,8), I=1,40) / 912.2D0,926.3D0,1174.0D0,674.3D0,
$-442.1D0,-125.1D0,125.4D0,0.0D0,-246.8D0,1.0D0,-72.58D0,6*1.0D0,
$-362.3D0,5*1.0D0,1953.0D0,6*1.0D0,772.5D0,9*1.0D0 /
 DATA (AA(I,9), I=1,40) / 476.4D0,524.5D0,25.77D0,-52.1D0,84.0D0,
$23.39D0,-195.4D0,-158.8D0,0.0D0,128.0D0,372.2D0,1.0D0,52.38D0,
$3*1.0D0,-399.1D0,-51.54D0,-287.5D0,-297.8D0,286.3D0,423.2D0,
$552.1D0,372.0D0,128.1D0,-142.6D0,1.0D0,303.7D0,160.6D0,317.5D0,
$1.0D0,138.0D0,-142.6D0,443.6D0,110.4D0,1.0D0,-8.671D0,1.0D0,
$97.04D0,1.0D0 /
 DATA (AA(I,10), I=1,40) / 677.0D0,3*1.0D0,441.8D0,306.4D0,
$-257.3D0,1.0D0,-37.36D0,0.0D0,1.0D0,1.0D0,-7.838D0,7*1.0D0,
$-47.51D0,19*1.0D0 /
 DATA (AA(I,11), I=1,40) / 232.1D0,4.826D0,5.994D0,5688.0D0,
$101.1D0,-10.72D0,14.42D0,-442.8D0,-213.7D0,1.0D0,0.0D0,-261.1D0,
$461.3D0,1.0D0,136.0D0,3*1.0D0,-266.6D0,-256.3D0,1.0D0,-132.9D0,
$176.5D0,129.5D0,-246.3D0,1.0D0,1.0D0,243.8D0,1.0D0,-146.3D0,
$152.0D0,21.92D0,1.0D0,1.0D0,41.57D0,1.0D0,-34.14D0,3*1.0D0 /
 DATA (AA(I,12), I=1,40) / 741.4D0,468.7D0,1.0D0,1.0D0,193.1D0,
$193.4D0,4*1.0D0,372.9D0,0.0D0,7*1.0D0,312.5D0,1.0D0,1.0D0,
$488.9D0,5*1.0D0,239.8D0,11*1.0D0 /
 DATA (AA(I,13), I=1,40) / 251.5D0,289.3D0,32.14D0,213.1D0,
$28.06D0,-180.6D0,540.5D0,1.0D0,5.202D0,304.1D0,-235.7D0,1.0D0,
$0.0D0,1.0D0,-49.3D0,4*1.0D0,-338.5D0,225.4D0,-197.7D0,-20.93D0,
$113.9D0,1.0D0,-94.49D0,1.0D0,112.4D0,63.71D0,1.0D0,9.207D0,
$476.6D0,736.4D0,1.0D0,-122.1D0,1.0D0,-209.3D0,1.0D0,-158.2D0,
$1.0D0 /
 DATA (AA(I,14), I=1,40) / 391.5D0,396.0D0,161.7D0,1.0D0,83.02D0,
$359.3D0,48.89D0,6*1.0D0,0.0D0,108.8D0,38.89D0,7*1.0D0,261.1D0,
$203.5D0,3*1.0D0,106.7D0,11*1.0D0 /
 DATA (AA(I,15), I=1,40) / 255.7D0,273.6D0,122.8D0,-49.29D0,
$42.70D0,266.0D0,168.0D0,3*1.0D0,-73.5D0,1.0D0,141.7D0,63.72D0,
$0.0D0,865.9D0,7*1.0D0,91.13D0,-108.4D0,15*1.0D0 /
```

```
 DATA (AA(I,16), I=1,40) / 206.6D0,658.8D0,90.49D0,23.5D0,-323.0D0,
$53.9D0,304.0D0,6*1.0D0,-41.11D0,-189.2D0,0.0D0,5*1.0D0,-141.4D0,
$-293.7D0,-126.0D0,1088.0D0,15*1.0D0 /
 DATA (AA(I,17), I=1,40) / 1245.0D0,1.0D0,668.2D0,764.7D0,-348.2D0,
$335.5D0,213.0D0,1.0D0,937.9D0,7*1.0D0,0.0D0,1.0D0,617.1D0,4*1.0D0,
$1301.0D0,323.3D0,1.0D0,5250.0D0,3*1.0D0,164.4D0,7*1.0D0,335.6D0,
$1.0D0 /
 DATA (AA(I,18), I=1,40) / 287.77D0,1.0D0,-4.449D0,52.8D0,170.0D0,
$580.5D0,459.0D0,-259.2D0,165.1D0,8*1.0D0,0.0D0,134.3D0,-313.5D0,
$1.0D0,587.3D0,18.98D0,309.2D0,16*1.0D0 /
 DATA (AA(I,19), I=1,40) / 597.0D0,405.9D0,212.5D0,6096.0D0,
$6.712D0,36.23D0,112.6D0,1.0D0,481.7D0,1.0D0,494.6D0,5*1.0D0,
$-216.8D0,-169.7D0,0.0D0,3*1.0D0,74.04D0,492.0D0,356.9D0,1.0D0,
$1.0D0,335.7D0,125.7D0,4*1.0D0,329.1D0,1.0D0,-42.31D0,298.4D0,
$3*1.0D0 /
 DATA (AA(I,20), I=1,40) / 663.5D0,730.4D0,537.4D0,603.8D0,199.0D0,
$-289.5D0,-14.09D0,1.0D0,669.4D0,1.0D0,660.2D0,-356.3D0,664.6D0,
$4*1.0D0,-153.7D0,1.0D0,0.0D0,326.4D0,1821.0D0,1346.0D0,689.0D0,
$12*1.0D0,2344.0D0,3*1.0D0 /
 DATA (AA(I,21), I=1,40) / 35.93D0,99.61D0,-18.81D0,-114.1D0,
$75.62D0,-38.32D0,325.4D0,1.0D0,-191.7D0,751.9D0,1.0D0,1.0D0,
$301.1D0,6*1.0D0,44.42D0,0.0D0,-84.53D0,-157.1D0,11.8D0,-314.9D0,
$1.0D0,1.0D0,-73.09D0,-27.94D0,3*1.0D0,1169.0D0,3*1.0D0,201.7D0,
$3*1.0D0 /
 DATA (AA(I,22), I=1,40) / 53.76D0,337.1D0,-144.4D0,1.0D0,-112.1D0,
$-102.5D0,370.4D0,1.0D0,-284.0D0,1.0D0,108.9D0,1.0D0,137.8D0,
$2*1.0D0,-73.85D0,1.0D0,-351.6D0,1.0D0,-183.4D0,108.3D0,0.0D0,
$0.0D0,17.97D0,7*1.0D0,-40.82D0,2*1.0D0,-215.0D0,5*1.0D0 /
 DATA (AA(I,23), I=1,40) / 24.9D0,4584.0D0,-231.9D0,-12.14D0,
$-98.12D0,-139.4D0,353.7D0,1.0D0,-354.6D0,1.0D0,-209.7D0,-287.2D0,
$-154.3D0,2*1.0D0,-352.9D0,1.0D0,-114.7D0,-15.62D0,76.75D0,
$249.2D0,2*0.0D0,51.9D0,3*1.0D0,-26.06D0,1.0D0,48.48D0,1.0D0,
$21.76D0,2*1.0D0,-343.6D0,1.0D0,85.32D0,3*1.0D0 /
 DATA (AA(I,24), I=1,40) / 104.3D0,5831.0D0,3.0D0,-141.3D0,143.1D0,
$-67.8D0,497.5D0,10000.0D0,-39.2D0,1.0D0,54.47D0,1.0D0,47.67D0,
$-99.81D0,71.23D0,-8.283D0,8455.0D0,-165.1D0,-54.86D0,212.7D0,
$62.42D0,56.33D0,-30.1D0,0.0D0,-255.4D0,-34.68D0,514.6D0,-60.71D0,
$1.0D0,-133.16D0,1.0D0,48.49D0,225.8D0,1.0D0,-58.43D0,1.0D0,
$143.2D0,-124.6D0,-186.7D0,1.0D0 /
 DATA (AA(I,25), I=1,40) / 321.5D0,959.7D0,538.2D0,-126.9D0,
$287.8D0,17.12D0,678.2D0,1.0D0,174.5D0,1.0D0,629.0D0,2*1.0D0,
$68.81D0,4350.0D0,-86.36D0,699.1D0,1.0D0,52.31D0,1.0D0,464.4D0,
$2*1.0D0,475.8D0,0.0D0,794.4D0,6*1.0D0,224.0D0,7*1.0D0 /
 DATA (AA(I,26), I=1,40) / 661.5D0,542.1D0,168.0D0,3629.0D0,
$61.11D0,75.14D0,220.6D0,1.0D0,137.5D0,3*1.0D0,95.18D0,10*1.0D0,
$490.9D0,-154.5D0,0.0D0,-85.12D0,3*1.0D0,481.3D0,64.28D0,125.3D0,
$174.4D0,2*1.0D0,313.8D0,3*1.0D0 /
 DATA (AA(I,27), I=1,40) / 543.0D0,1.0D0,194.9D0,4448.0D0,157.1D0,
$1.0D0,399.5D0,9*1.0D0,-62.73D0,6*1.0D0,534.7D0,1.0D0,533.2D0,
$0.0D0,13*1.0D0 /
 DATA (AA(I,28), I=1,40) / 153.6D0,76.302D0,52.07D0,-9.451D0,
$477.0D0,-31.09D0,887.1D0,1.0D0,216.1D0,1.0D0,183.0D0,1.0D0,
$140.9D0,5*1.0D0,230.9D0,1.0D0,450.1D0,1.0D0,116.6D0,132.2D0,
$3*1.0D0,0.0D0,8*1.0D0,167.9D0,3*1.0D0 /
 DATA (AA(I,29), I=1,40) / 184.4D0,1.0D0,-10.43D0,1.0D0,147.5D0,
     $37.84D0,2*1.0D0,-46.28D0,2*1.0D0,4.339D0,-8.538D0,-70.14D0,
     $4*1.0D0,21.37D0,1.0D0,59.02D0,7*1.0D0,0.0D0,5*1.0D0,85.7D0,
     $3*1.0D0,-71.0D0,1.0D0 /
      DATA (AA(I,30), I=1,40) / 354.55D0,1.0D0,-64.69D0,-20.36D0,
     $-120.5D0,1.0D0,188.0D0,1.0D0,-163.7D0,1.0D0,202.3D0,11*1.0D0,
     $-64.38D0,546.7D0,5*1.0D0,0.0D0,10*1.0D0 /
      DATA (AA(I,31), I=1,40) / 3025.0D0,1.0D0,210.4D0,4975.0D0,
     $-318.9D0,1.0D0,0.0D0,-638.2D0,2*1.0D0,-101.7D0,1.0D0,-20.11D0,
     $3*1.0D0,125.3D0,8*1.0D0,139.8D0,4*1.0D0,0.0D0,3*1.0D0,535.8D0,
     $3*1.0D0,-191.7D0,1.0D0 /
      DATA (AA(I,32), I=1,40) / 335.8D0,1.0D0,113.3D0,1.0D0,313.5D0,
     $3*1.0D0,53.59D0,1.0D0,148.3D0,1.0D0,-149.5D0,8*1.0D0,177.6D0,
     $86.4D0,247.8D0,1.0D0,304.3D0,5*1.0D0,0.0D0,8*1.0D0 /
      DATA (AA(I,33), I=1,40) / 479.5D0,1.0D0,-13.59D0,-171.3D0,
     $133.4D0,1.0D0,440.0D0,1.0D0,245.2D0,3*1.0D0,-202.3D0,7*1.0D0,
     $-125.9D0,2*1.0D0,41.94D0,-60.7D0,10.17D0,6*1.0D0,0.0D0,7*1.0D0 /
      DATA (AA(I,34), I=1,40) / 298.9D0,523.6D0,6*1.0D0,-246.6D0,
     $9*1.0D0,-203.0D0,6*1.0D0,-27.7D0,7*1.0D0,0.0D0,4*1.0D0,6.699D0,
     $1.0D0 /
      DATA (AA(I,35), I=1,40) / 526.5D0,1.0D0,169.9D0,4284.0D0,-202.1D0,
     $-399.3D0,-139.0D0,1.0D0,-44.58D0,1.0D0,-21.13D0,1.0D0,172.1D0,
     $8*1.0D0,215.0D0,363.7D0,337.7D0,4*1.0D0,31.66D0,1.0D0,-417.2D0,
     $3*1.0D0,0.0D0,3*1.0D0,136.6D0,1.0D0 /
      DATA (AA(I,36), I=1,40) / 689.0D0,5*1.0D0,160.8D0,11*1.0D0,
     $81.57D0,16*1.0D0,0.0D0,4*1.0D0 /
      DATA (AA(I,37), I=1,40) / -0.505D0,237.3D0,69.11D0,1.0D0,253.9D0,
     $-21.22D0,2*1.0D0,-44.42D0,1.0D0,-19.28D0,1.0D0,145.6D0,5*1.0D0,
     $-19.14D0,-90.87D0,-58.77D0,1.0D0,-79.54D0,-86.85D0,1.0D0,48.4D0,
     $1.0D0,-47.37D0,8*1.0D0,0.0D0,3*1.0D0 /
      DATA (AA(I,38), I=1,40) / 125.8D0,1.0D0,389.3D0,101.4D0,44.78D0,
     $-48.25D0,17*1.0D0,215.2D0,13*1.0D0,0.0D0,2*1.0D0 /
      DATA (AA(I,39), I=1,40) / 485.3D0,320.4D0,245.6D0,5629.0D0,
     $-143.9D0,-172.4D0,319.0D0,1.0D0,-61.7D0,3*1.0D0,254.8D0,3*1.0D0,
     $-293.1D0,6*1.0D0,498.6D0,4*1.0D0,78.92D0,1.0D0,302.2D0,2*1.0D0,
     $-119.8D0,-97.71D0,3*1.0D0,0.0D0,1.0D0 /
      DATA (AA(I,40), I=1,40) / -2.859D0,38*1.0D0,0.0D0 /
C
      OPEN(7,FILE='UNIFAC.OUT')
C
C     READ INPUT FROM SCREEN
C
      PRINT*, 'INPUT REQUIRED'
      PRINT*, 'WHAT IS THE NAME OF THE COMPOUND?  '
      READ(*,10) NAME
10    FORMAT(A20)
      PRINT*, 'WHAT IS THE MOLECULAR WEIGHT?  '
      READ(*,*) MW
      PRINT*, 'HOW MANY DIFFERENT FUNCTIONAL GROUPS ARE THERE?  '
      READ(*,*) NUM
      DO 20 I=1,NUM
       PRINT*, 'FOR FUNCTIONAL GROUP NUMBER ',I
       PRINT*, ' '
       PRINT*, 'WHAT IS THE MAIN GROUP NUMBER (INTEGER),'
       PRINT*, 'THE COMPONENT NUMBER (INTEGER),'
       PRINT*, 'AND HOW MANY OF THIS SPECIFIC GROUP ARE PRESENT ON THE C
     $OMPOUND (REAL)?'
       PRINT*, ' '
       READ(*,*) MGN(I),CN(I),VK(I)
20    CONTINUE
      PRINT*, 'HOW MANY DIFFERENT TEMPERATURES DO YOU WANT SOLUBILITIES
     $FOR? '
      READ(*,*) NT
      DO 25 I=1,NT
       PRINT*, 'WHAT IS TEMPERATURE ',I,' ? '
       READ(*,*) T(I)
25    CONTINUE
C
C     ASSIGN VAN DER WAALS VOLUME AND SURFACE AREA FROM DATA BASE
C
      PRINT*, 'STARTING CALCULATIONS '
      DO 30 I=1,NUM
       J=CN(I)
       R(I)=RR(J)
       Q(I)=QQ(J)
30    CONTINUE
C
C     CALCULATE TOTAL VOLUME AND SURFACE AREAS ON MOLECULE
C
      R1=0.0D0
      Q1=0.0D0
      DO 40 I=1,NUM
       R1=R1+VK(I)*R(I)
       Q1=Q1+VK(I)*Q(I)
40    CONTINUE
       R2=0.92D0
       Q2=1.4D0
C
C     CALCULATE UNIFAC PARAMETER L
C
      L1=5.0D0*(R1-Q1)-(R1-1.0D0)
      L2=5.0D0*(R2-Q2)-(R2-1.0D0)
C
C  CALCULATE COMBINATORIAL PART OF THE ACTIVITY COEFFICIENT FOR SOLUTE
C
      LNYC=DLOG(R1/R2)+5.0D0*Q1*DLOG(Q1*R2/Q2/R1)+L1-(R1/R2)*L2
C
C     ASSIGN GROUP INTERACTION PARAMETERS FROM DATA BASE
C
      DO 60 I=1,NUM
       DO 50 J=1,NUM
        MMX=MGN(I)
        MMY=MGN(J)
        A(I,J)=AA(MMX,MMY)
        IF (AA(I,J) .EQ. 1.0D0) THEN
         WRITE(7,45) I,J
45       FORMAT(1X,'THE GROUP INTERACTION PARAMETER FOR COMPONENTS',/,
     $   1X,I2,' AND ',I2,' IS NOT AVAILABLE.  EXECUTION ABORTED')
         PRINT*, 'THE GROUP INTERACTION PARAMETER FOR COMPONENTS'
         PRINT*, I,' AND ',J,' ARE NOT AVAILABLE.  EXECUTION ABORTED'
         GOTO 3000
        ENDIF
50     CONTINUE
60    CONTINUE
C
C     ASSIGN GROUP INTERACTION PARAMETERS FOR WATER FROM DATA BASE
C
      DO 65 I=1,NUM
       MMX=MGN(I)
       A(I,NUM+1)=AA(MMX,7)
       IF (AA(MMX,7) .EQ. 1.0D0) THEN
        WRITE(7,45) MMX,7.0D0
        PRINT*, 'THE GROUP INTERACTION PARAMETER FOR COMPONENTS'
        PRINT*, MMX,' AND 7 ARE NOT AVAILABLE.  EXECUTION ABORTED'
        GOTO 3000
        ENDIF
        A(NUM+1,I)=AA(7,MMX)
        IF (AA(7,MMX) .EQ. 1.0D0) THEN
        WRITE(7,45) 7.0D0,MMX
        PRINT*, 'THE GROUP INTERACTION PARAMETER FOR COMPONENTS'
        PRINT*, '7 AND ',MMX,' ARE NOT AVAILABLE.  EXECUTION ABORTED'
        GOTO 3000
       ENDIF
65    CONTINUE
C
C     CALCULATE UNIFAC PARAMETER FROM GROUP INTERACTION PARAMETERS (PSI)
C
      DO 2000 II=1,NT
       PRINT*, 'CALCULATING FOR TEMPERATURE = ',T(II)
       DO 80 I=1,NUM+1
        DO 70 J=1,NUM+1
         YY(I,J)=DEXP(-A(I,J)/(T(II)+273.0D0))
70      CONTINUE
80     CONTINUE
C
C     CALCULATION OF GROUP FRACTION FOR SOLUTE (SOLVENT=0)
C
       VKT=0.0D0
       DO 90 I=1,NUM
        VKT=VKT+VK(I)
90     CONTINUE
       DO 100 I=1,NUM
        X(I)=VK(I)/VKT
100    CONTINUE
       X(NUM+1)=0.0D0
C
C     CALCULATION OF GROUP SURFACE AREA FRACTION (THETA)
C
       QT=0.0D0
       DO 110 I=1,NUM
        QT=QT+Q(I)*X(I)
110    CONTINUE
       DO 120 I=1,NUM
        GSAF(I)=Q(I)*X(I)/QT
120    CONTINUE
       GSAF(NUM+1)=0.0D0
```

```
C
C     CALCULATE GROUP ACTIVITY COEFFICIENT FOR PURE SOLUTE (GAMMA)
C
       DO 150 K=1,NUM
        SUM2=0.0D0
        SUM3=0.0D0
        DO 140 I=1,NUM
         SUM1=0.0D0
         DO 130 J=1,NUM
          SUM1=SUM1+GSAF(J)*YY(J,I)
130      CONTINUE
         SUM2=SUM2+GSAF(I)*YY(K,I)/SUM1
         SUM3=SUM3+GSAF(I)*YY(I,K)
140     CONTINUE
        GAC(K)=Q(K)*(1.0D0-DLOG(SUM3)-SUM2)
150    CONTINUE
C
C     CALCULATE GROUP ACTIVITY COEFFICIENTS FOR PURE WATER SOLUTION
C
       DO 180 I=1,NUM
        GACW(I)=Q(I)*(1.0D0-DLOG(YY(NUM+1,I))-YY(I,NUM+1))
180    CONTINUE
C
C   CALCULATE THE RESIDUAL PART OF THE ACTIVITY COEFFICIENT FOR SOLUTE
C
       LNYR=0.0D0
       DO 190 I=1,NUM
        LNYR=LNYR+VK(I)*(GACW(I)-GAC(I))
190    CONTINUE
C
C     COMBINE PARTS OF ACTIVITY COEFFICIENT
C
       AC=LNYC+LNYR
       ACT=DEXP(AC)
C
C     CALCULATE SOLUBILITY TWO WAYS
C
       SOL1=55.5D0/ACT
       SOL2=1.20D0+0.782D0*DLOG10(1.0D0/ACT)
       SOL2=10.0D0**SOL2
C
C     CONVERT TO mg/L
C
       SOL1=SOL1*MW*1000.0D0
       SOL2=SOL2*MW*1000.0D0
C
C     WRITE TO FILE
C
      PRINT*, 'PRINTING RESULTS FOR TEMPERATURE= ',T(II)
      IF (II .EQ. 1) THEN
       WRITE(7,200) NAME,MW
200    FORMAT(1X,'DETERMINATION OF SOLUBILITY USING UNIFAC DERIVED',1X,
     $ 'ACTIVITY COEFFICIENTS',//,'COMPOUND = ',A20,
     $ /,'MOLECULAR WEIGHT EQUALS ',F7.2,//)
       WRITE(7,205)
```

```
205    FORMAT(1X,'INPUT CHECK',//)
       DO 220 I=1,NUM
        WRITE(7,210) MGN(I),CN(I),VK(I),R(I),Q(I)
210     FORMAT('MAIN GROUP NUMBER EQUALS ',I2,/,
     $  'COMPONENT GROUP NUMBER EQUALS ',I2,/,
     $  'NUMBER OF TIMES THIS FUNCTIONAL GROUP IS ON MOLECULE ',F4.1,/,
     $  'VAN DER WAALS VOLUME EQUALS ',F10.4,/,
     $  'VAN DER WAALS SURFACE AREA EQUALS ',F10.4,//)
220    CONTINUE
       WRITE(7,230)
230    FORMAT('RESULTS ',///,'TEMPERATURE',32X,'SOLUBILITY (mg/L)',//,
     $' DEGREES C ',T16,'ACTIVITY COEFF',T35,
     $'1 ST CORRELATION',T56,'2 ND CORRELATION',/,T58,'Banerjee°s',//)
      ENDIF
      WRITE(7,240) T(II),ACT,SOL1,SOL2
240   FORMAT(T2,F7.2,T19,1E8.3,T35,F12.2,T56,F12.2)
2000  CONTINUE
3000  CONTINUE
      STOP
      END
```

Sample Output for UNIFAC Program

```
 DETERMINATION OF SOLUBILITY USING UNIFAC DERIVED ACTIVITY COEFFICIENTS

COMPOUND = TRICHLOROETHENE
MOLECULAR WEIGHT EQUALS  131.29


 INPUT CHECK


MAIN GROUP NUMBER EQUALS  2
COMPONENT GROUP NUMBER EQUALS  9
NUMBER OF TIMES THIS FUNCTIONAL GROUP IS ON MOLECULE  1.0
VAN DER WAALS VOLUME EQUALS      0.6605
VAN DER WAALS SURFACE AREA EQUALS      0.4850


MAIN GROUP NUMBER EQUALS 21
COMPONENT GROUP NUMBER EQUALS 46
NUMBER OF TIMES THIS FUNCTIONAL GROUP IS ON MOLECULE  1.0
VAN DER WAALS VOLUME EQUALS      1.2380
VAN DER WAALS SURFACE AREA EQUALS      0.9520


MAIN GROUP NUMBER EQUALS 22
COMPONENT GROUP NUMBER EQUALS 50
NUMBER OF TIMES THIS FUNCTIONAL GROUP IS ON MOLECULE  1.0
VAN DER WAALS VOLUME EQUALS      1.8016
VAN DER WAALS SURFACE AREA EQUALS      1.4480


RESULTS


TEMPERATURE                                    SOLUBILITY (mg/L)

 DEGREES C      ACTIVITY COEFF       1 ST CORRELATION       2 ND CORRELATION
                                                                Banerjee°s


    0.00          .103E+05                704.60                1509.49
    5.00          .948E+04                768.82                1616.03
   10.00          .871E+04                836.64                1726.48
   13.80          .818E+04                890.64                1813.03
   15.00          .802E+04                908.14                1840.82
   20.00          .741E+04                983.38                1959.04
   21.00          .729E+04                998.88                1983.15
   25.00          .686E+04               1062.41                2081.13
   30.00          .636E+04               1145.30                2207.06
   35.00          .591E+04               1232.10                2336.81
   40.00          .551E+04               1322.86                2470.36
   45.00          .514E+04               1417.62                2607.70
   50.00          .481E+04               1516.43                2748.79
```

APPENDIX VI. POLANYI POTENTIAL COMPUTER CODE.

```
C
C     THIS PROGRAM WILL ESTIMATE THE FREUNDLICH K'S AND 1/N'S FOR
C     HYDROPHOBIC COMPOUNDS FOR A SPECIFIC CARBON.
C     USING THE CURVE FITTING EQUATION ln Y = AX**B + ln C
C
C     WRITTEN BY:  THOMAS FRANCIS SPETH
C
C     VARIABLE DEFINITIONS
C
C     CHECK = CHECK TO SEE IS THE PROGRAM SHOULD BE RUN AGAIN
C     DEN   = DENSITY OF COMPOUND (g/ml)
C     DIFC  = DIFFERENCE IN C - USED TO CALCULATE INTERCEPT
C     DIFQ  = DIFFERENCE IN Q - USED TO CALCULATE INTERCEPT
C     FAC   = PACTOR TO CALCULATE THE INTERCEPT
C     INT   = INTERCEPT OR KG OF COMPOUND
C     INTRCPT= INTERCEPT OF THE CORRELATION CURVE (ml/g)
C     KG    = FREUNDLICH K (ug/g)(L/ug)**1/n
C     KM    = FREUNDLICH K (um/g)(L/ug)**1/n
C     MW    = MOLECULAR WEIGHT OF COMPOUND
C     NAME  = NAME OF COMPOUNDS
C     NC    = NUMBER OF COMPOUNDS
C     POWER = POWER OF CORRELATION CURVE
C     Q1    = SOLID-PHASE CONC. AT LIQ.-PHASE CONC.= 100 ug/L  (ug/g)
C     Q2    = SOLID-PHASE CONC. AT LIQ.-PHASE CONC.= 200 ug/L  (ug/g)
C     R     = IDEAL GAS CONSTANT (1.987 cal/gmol/K)
C     SLOPE = SLOPE OF THE CORRELATION CURVE
C     SLP   = SLOPE OR 1/n OF COMPOUND
C     SOL   = SOLUBILITY OF COMPOUND (mg/L)
C     T     = TEMPERATURE (C)
C
C     INPUT ITEMS
C
C     CARBON, SLOPE, POWER, INTERCPT
C     NAME(1),  MW(1),  DEN(1),  SOL(1),  T(1)
C     ....      ..      ...      ...      .
C     NAME(NC), MW(NC), DEN(NC), SOL(NC), T(NC)
C
C     PROGRAM
C
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DOUBLE PRECISION INT,INTRCPT,MW,KG,KM,LOW
      CHARACTER*20 NAME,CARBON,CHECK
      OPEN(7,FILE='POL3.OUT')
C
C     READ INPUT
C
      PRINT*, 'READING INPUT'
      PRINT*, ' '
      PRINT*, 'WHAT IS THE CARBON TYPE?  '
      READ(*,5) CARBON
5     FORMAT(A20)
      PRINT*,'WHAT ISTHE SLOPE,THE POWER, AND THE INTERCEPTIN'
      PRINT*, '(mL/g) OF THE CORRELATION CURVE?  '
      READ(*,*) SLOPE,POWER,INTRCPT
10    PRINT*, 'WHAT IS THE NAME OF THE SOLUTE ? '
      READ(*,5) NAME
      PRINT*, 'WHAT IS THE MOLECULAR WEIGHT AND DENSITY OF THE SOLUTE? '
      READ(*,*) MW,DEN
      PRINT*, 'WHAT TEMPERATURE DO YOU WANT THE PREDICTION FOR, AND '
      PRINT*, 'WHAT SOLUBILITY CORRESPONDS TO THIS TEMPERATURE ?  '
      READ(*,*) T,SOL
      PRINT*, 'WHAT CONCENTRATION RANGE DO YOU WANT THE SOLUBILITIES '
      PRINT*, 'AT?  (LOW TO HIGH IN (ug/L)) '
      READ(*,*) C1,C2
      R=1.987D0
C
C     CALCULATE SOLID-PHASE CONC. AT TWO POINTS
C      K AND 1/N ARE A FUNCTION OF CONC. IF CORR. CURVE IS NONLINEAR
C
      PRINT*, 'CALCULATING'
      INTRCPT=DLOG(INTRCPT)
       Q1=1.0D6*DEN*DEXP(SLOPE*(R*(T+273.0D0)*DLOG(SOL
     $ *1000.0D0/C1)*DEN/MW)**POWER+INTRCPT)
       Q2=1.0D6*DEN*DEXP(SLOPE*(R*(T+273.0D0)*DLOG(SOL
     $ *1000.0D0/C2)*DEN/MW)**POWER+INTRCPT)
C
C     FIND SLOPE AND INTERCEPT FROM THE 2 PT. ISOTHERMS
C
       SLP=(DLOG(Q2)-DLOG(Q1))/(DLOG(C2)-DLOG(C1))
       DIFQ=DLOG(Q2)-DLOG(Q1)
       DIFC=DLOG(C2)-DLOG(C1)
       FAC=LOG(C1)/DIFC
       INT=DLOG(Q1)-FAC*DIFQ
       KG=DEXP(INT)
       KM=KG/MW*MW**SLP
       INTRCPT=DEXP(INTRCPT)
C
C     PRINT OUT RESULTS
C
      IF (CHECK .EQ. 'YES' .OR. CHECK .EQ. 'yes') GOTO 105
      PRINT*, 'PRINTING RESULTS'
      WRITE(7,100) CARBON,SLOPE,POWER,INTRCPT
100   FORMAT(1X,'PREDICTION OF K°s AND 1/n°s USING A CORRELATION CURVE'
     $,//,1X,'CARBON TYPE = ',A20,//,1X,'EQUATION OF CURVE :',2X,
     $'ln W = A (E/V)**B + ln C',//,1X,'WHERE',/,1X,'A = ',1G12.5,/,
     $1X,'B = ',1G12.5,/,1X,'C = ',1G12.5,///)
105   WRITE(7,110)
110   FORMAT(1X,'COMPOUND',T20,
     $'K (ug/g)(L/ug)**1/n',T42,'K (um/g)(L/um)**1/n',T65,'1/n',//)
       WRITE(7,120) NAME,KG,KM,SLP,T,SOL,MW,DEN,C1,C2,Q1,Q2
120    FORMAT(1X,A20,T22,1G12.6,T45,1G12.7,T63,1G10.4,//,1X,
     $ 'TEMPERATURE = ',1G12.6,T50,' degrees C',/,1X,'SOLUBILITY = ',
     $ 1G12.6,T50,' (mg/L)',/,1X,'MOLECULAR WEIGHT = ',F9.3,/,
     $ 1X,'DENSITY = ',1G12.6,T50,' (g/ml)',/,
     $ 1X,'LIQIUD PHASE CONC. (LOW) = ',1G12.6,T50,' (ug/L)',/,
     $ 1X,'LIQIUD PHASE CONC. (HIGH) = ',1G12.6,T50,' (ug/L)',/,
     $ 1X,'SOLID PHASE CONC. (LOW) = ',E8.2,T50,' (ug/g)',/,
     $ 1X,'SOLID PHASE CONC. (HIGH) = ',E8.2,T50,' (ug/g) ',////)
```

```
C
C     CHECK TOO SEE IF THE PROGRAM SHOULD BE RUN AGAIN
C
      PRINT*, 'DO YOU WISH TO RUN THE PROGRAM AGAIN USING THE'
      PRINT*, 'SAME CORRELATION CURVE ?  '
      READ(*,125) CHECK
125   FORMAT(A3)
      IF (CHECK .EQ. 'YES' .OR. CHECK .EQ. 'yes') GOTO 10
C
      STOP
      END
```

Sample Output - Polanyl Potential Theory

```
PREDICTION OF K°s AND 1/n°s USING A CORRELATION CURVE

CARBON TYPE = f-400

EQUATION OF CURVE :  ln W = A (E/V)**B + ln C

WHERE
A = -0.17180E-01
B =   1.2426
C =  0.52940


COMPOUND          K (ug/g)(L/ug)**1/n  K (um/g)(L/um)**1/n    1/n


dce                   251.882              43.12784          0.6142

TEMPERATURE =  10.0000                           degrees C
SOLUBILITY =  1921.00                            (mg/L)
MOLECULAR WEIGHT =     96.940
DENSITY =  1.28000                               (g/ml)
LIQIUD PHASE CONC. (LOW) =  10.0000              (ug/L)
LIQIUD PHASE CONC. (HIGH) =  5000.00             (ug/L)
SOLID PHASE CONC. (LOW) = 0.10E+04               (ug/g)
SOLID PHASE CONC. (HIGH) = 0.47E+05              (ug/g)



COMPOUND          K (ug/g)(L/ug)**1/n  K (um/g)(L/um)**1/n    1/n


tce                   2891.39              208.7002          0.4611

TEMPERATURE =  10.0000                           degrees C
SOLUBILITY =  836.600                            (mg/L)
MOLECULAR WEIGHT =   131.290
DENSITY =  1.46200                               (g/ml)
LIQIUD PHASE CONC. (LOW) =  10.0000              (ug/L)
LIQIUD PHASE CONC. (HIGH) =  3000.00             (ug/L)
SOLID PHASE CONC. (LOW) = 0.84E+04               (ug/g)
SOLID PHASE CONC. (HIGH) = 0.12E+06              (ug/g)



COMPOUND          K (ug/g)(L/ug)**1/n  K (um/g)(L/um)**1/n    1/n


pce                   13229.4              525.6793          0.3689
```

```
TEMPERATURE =  10.0000                               degrees C
SOLUBILITY =  322.100                                (mg/L)
MOLECULAR WEIGHT =   165.830
DENSITY =  1.62000                                   (g/ml)
LIQIUD PHASE CONC. (LOW) =  10.0000                  (ug/L)
LIQIUD PHASE CONC. (HIGH) =  2000.00                 (ug/L)
SOLID PHASE CONC. (LOW) = 0.31E+05                   (ug/g)
SOLID PHASE CONC. (HIGH) = 0.22E+06                  (ug/g)
```

APPENDIX VII. EFFECT OF TEMPERATURE ON ISOTHERMS USING THE CLAUSIUS-CLAPEYRON EQUATION - DERIVATION AND COMPUTER PROGRAM

The Clausius-Clapeyron equation relates the change in concentration with the change in temperature.

$$Q_{iso} = R*T^2*(\partial \ln C/\partial T)_q \qquad \text{(VII-8)}$$

Where,

C = liquid-phase concentration

T = absolute temperature

R = gas constant

Q_{iso} = isosteric heat of adsorption

q = solid-phase concentration

If it is integrated assuming constant q and Q_{iso}, the following equation is obtained.

$$Q_{iso} = -R*(\ln C_1 - \ln C_2)/(1/T_1 - 1/T_2) \qquad \text{(VII-9)}$$

Solving for C_2,

$$C_2 = C_1*\exp((1/T_1 - 1/T_2)*Q_{iso}/R) \qquad \text{(VII-10)}$$

The only unknown in predicting a liquid-phase concentration at a different temperature is the isosteric heat of adsorption. Q_{iso}. To determine Q_{iso} the Clausius-Clapeyron equation is again used.

$$Q_{iso} = R*T^2*(\partial \ln C/\partial T)_q \qquad \text{(VII-11)}$$

As stated in this thesis, the modified Freundlich equation is:

$$Q = K' \ (C/C_s)^{1/n} \qquad \text{(VII-12)}$$

Solving the modified Freundlich equation for C and substituting it into the Clausius-Clapeyron Equation, the following equation is obtained.

$$Q_{iso} = R*T^{2}*\ \partial(\ln(C_{s}*(Q/K')^{n}))/\ \partial T \tag{VII-13}$$

Since Cs, Q, and n are only functions of temperature, the partial derivatives in Equation VII-13 can be replaced by ordinary derivatives.

$$Q_{iso} = R*T^{2}*(\ d\ln C_{s}/dT + d(n*\ln Q)/dT - d(n*\ln K')/dT) \tag{VII-14}$$

By the product rule.

$$d(n*\ln Q)/dT = \ln Q\ dn/dT + n*d\ln Q/dT \tag{VII-15}$$

and,

$$d(n*\ln K')/dT = \ln K'dn/dT + n*d\ln K'/dT \tag{VII-16}$$

Therefore, Equation VII-13 becomes:

$$Q_{iso} = R*T^{2}*(n*d\ln K'/dT-\ln K'\ dn/dT+\ln Q\ dn/dT+d\ln Cs\ /dT) \tag{VII-17}$$

If a and A are temperature independent, the k'=A/a is also temperature independent. Consequently, dn/dT can be given as:

$$dn/dT = d(1/(a*R*T)/dT = -1/a*R*T^{2} = -n/T \tag{VII-18}$$

Equation VII-17 becomes.

$$Q_{iso} = n*R*T*(\ln k' - \ln Q + T/n*d(\ln Cs/dT)) \tag{VII-19}$$

By taking the natural logarithm of the modified Freundlich equation.

$$\ln Q = \ln\ (A/a) - a*\varepsilon_{eq} = \ln K' - a*\varepsilon_{eq} \tag{VII-20}$$

and remembering that

$$a = 1/(n*R*T) \qquad \text{(VII-21)}$$

$$Q_{iso} = n*R*T*(\ln K' - \ln K' + \varepsilon_{eq}/(n*R*T) + T/n*(d(\ln Cs/dT)) \qquad \text{(VII-22)}$$

or,

$$Q_{iso} = \varepsilon_{eq} + R*T^{2}*d \ln Cs/dT \qquad \text{(VII-23)}$$

Equation VIII-23 is then substituted into Equation VII-10 to obtain the liquid phase concentration at the second temperature. The solid phase concentration remains constant.

PROGRAM TO PREDICT THE EFFECT OF TEMPERATURE ON ISOTHERMS

```
C
C                 ISOTHERM CHANGES DUE TO TEMPERATURE
C
C
C     THIS PROGRAM WILL PREDICT THE DEPENDENCE OF TEMPERATURE ON
C     ISOTHERMS.  IT WILL DO THIS BY USING THE VAN'T HOFF EQUATION
C     AS DISCUSSED IN THE PREVIOUS DISCUSSION.  THE PROGRAM
C     REQUIRES SOLUBILITIES AT THE TEMPERATURE OF THE KNOWN
C     ISOTHERM AND THE TEMPERATURE OF THE PREDICTED ISOTHERM.
C
C     THE FOLLOWING PROGRAM IS WRITTEN IN DOUBLE PRECISION.
C
C     PROGRAM WRITTEN BY:  THOMAS FRANCIS SPETH
C
C            ********VARIABLE DEFINITIONS**********
C
C     ALT   = COMPONENT OF CAIM AND CNEW
C     CE    = KNOWN BULK LIQUID CONCENTRATION (ug/L)
C     CNEW  = BULK LIQUID CONCENTRATION PREDICTED-VAN HOFT (ug/L)
C     COMP  = COMPOUNDS NAME 10 LETTERS
C     CS1   = SOLUBILITY AT THE TEMP. OF THE KNOWN ISOTHERM (mg/L)
C     CS2   = SOLUBILITY AT THE PREDICTED ISOTHERM (mg/L)
C     CT    = TOTAL MOLAR CONCENTRATION (mmol/ml)
C     E     = ADSORPTION POTENTIAL (cal/gmol)
C     HDISS = HEAT OF DISSOLUTION (VAN HOFT) (cal/gmol)
C     I     = COUNTER
C     LDEN  = LIQUID DENSITY (g/cm3)
C     MW    = MOLECULAR WEIGHT
C     MVOL  = MOLAR VOLUME OF SOLUTE (ml/gmol)
C     NDATA = NUMBER OF DATA POINTS
C     QE    = ADSORBENT EQUILIBRIUM CONCENTRATION KNOWN (ug/g)
C     QISOV = HEAT OF ADSORPTION USING VAN HOFT (cal/gmol)
C     R     = GAS CONSTANT (1.987 cal/gmol/K)
C     T1    = TEMPERATURE OF KNOWN ISOTHERM (C)
C     T2    = TEMPERATURE OF THE TO BE PREDICTED ISOTHERM (C)
C     TS1   = TEMPERATURE OF FIRST REFERNCE SOLUBILITY
C     TS2   = TEMPERATURE OF SECOND REFERENCE SOLUBILITY
C     X     = MOLE FRACTION OF SOLUTE
C     XS    = MOLE FRACTION OF SATURATED SOLUTE
C
C
C                        SAMPLE INPUT
C
C
C     COMP
C     NDATA
C     CS1,TS1
C     CS2,TS2
C     MW
C     LDEN
C     CE(I),    QE(I)
C     ..        ..
```

```
C     CE(NDATA),QE(NDATA)
C
C
C               **********PROGRAM***********
C
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DOUBLE PRECISION MW,LDEN,MVOL
      CHARACTER*10 COMP
      DIMENSION CE(30),QE(30),E(30),QISOV(30),CNEW(30)
C
      OPEN(4,FILE='TFS.DAT')
      OPEN(7,FILE='TFS.OUT')
C
      R=1.9870D0
      CT=55.555550D0
C
C                  READ IN CONSTANTS
C
      PRINT*, 'READING INPUT'
      READ(4,*) COMP
      READ(4,*) NDATA
      READ(4,*) CS1,TS1
      READ(4,*) CS2,TS2
      TS1=TS1+273.0D0
      TS2=TS2+273.0D0
      READ(4,*) MW
      READ(4,*) LDEN
      DO 100 I=1,NDATA
       READ(4,*) CE(I),QE(I)
100   CONTINUE
C
      MVOL=MW/LDEN
      CS1=CS1/1000.0D0/MW
      CS2=CS2/1000.0D0/MW
      XS=CS1/CT
C
C       CALCULATION OF ADSORPTION POTENTIAL (RST+VAN'T HOFF)
C
      DO 200 I=1,NDATA
       X=CE(I)/CT*1.0D-6/MW
       E(I)=R*TS1*DLOG(XS/X)
200   CONTINUE
C
C      CALCULATION OF THE HEAT OF DISSOLUTION (VAN'T HOFF)
C
      HDISS=R*(TS1*TS2/(TS2-TS1))*DLOG(CS2/CS1)
C
C     CALCULATION OF HEAT OF ADSORPTION (VAN'T HOFF)
C
      DO 400 I=1,NDATA
       QISOV(I)=E(I)+HDISS
400   CONTINUE
C
C     CALCULATION OF THE NEW CONCENTRATIONS (VAN'T HOFF)
C
```

```
      DO 500 I=1,NDATA
       ALT=1.0D0/TS1-1.0D0/TS2
       CNEW(I)=CE(I)*DEXP(QISOV(I)/R*ALT)
500   CONTINUE
C
C        CHANGE TS1, AND TS2 BACK TO DEGREES C
C              AND SOLUBILITIES TO mg/L
C
      TS1=TS1-273.0D0
      TS2=TS2-273.0D0
      CS1=CS1*MW*1000.0D0
      CS2=CS2*MW*1000.0D0
C
C                  PRINT OUT
C
      PRINT*, 'PRINTING OUTPUT'
      WRITE(7,900) COMP,NDATA,TS1,TS2,CS1,CS2,MW,LDEN
900    FORMAT(1X,'COMPOUND = ',A10,/,
     $1X,'NUMBER OF DATA POINTS = ',I2,/,
     $1X,'TEMPERATURE OF THE KNOWN ISOTHERM = ',F8.2,' C',/,
     $1X,'TEMPERATURE OF THE UNKNOWN ISOTHERN = ',F8.2,' C',/,
     $1X,'SOLUBILITY OF KNOWN ISOTHERM= ',F8.2,' mg/L',/,
     $1X,'SOLUBILITY OF UNKNOWN ISOTHERM= ',F8.2,' mg/L',/,
     $1X,'MOLECULAR WEIGHT = ',F8.2,/,
     $1X,'LIQIUD DENSITY = ',F8.4,' g/cm3',///)
      WRITE(7,910)
910   FORMAT(T12,'ADSORPTION',T30,'HEAT OF'
     $,/,1X,'DATA',T12,'POTENTIAL',T29,'ADSORPTION'
     $,/,1X,'POINT',T12,
     $'(cal/gmol)',T29,'(cal/gmol)',/)
      DO 930 I=1,NDATA
       WRITE(7,920) I,E(I),QISOV(I)
920    FORMAT(1X,I2,T12,F9.3,T29,F9.1)
930   CONTINUE
      WRITE(7,940) TS1,TS2
940   FORMAT(///,1X,T18,'KNOWN',T36,'PREDICTION',
     $/,T16,'AT ',F5.1,' C',T36,'AT ',F5.1,' C',
     $/,1X,'DATA',/,1X,'POINT',T11,'C (ug/L)',T24,'Q (ug/g)',T38,
     $'C (ug/L)',/)
      DO 960 I=1,NDATA
       WRITE(7,950) I,CE(I),QE(I),CNEW(I)
950    FORMAT(1X,I2,T10,F9.3,T23,F10.2,T36,F9.3)
960   CONTINUE
      STOP
      END
```

Sample Input to Determine the Effect of Temperature on Isotherms

```
'TCE'
14
836.6,10.0
1062.4,21.0
131.29
1.462
360.0,39281.0
5.6,6941.7
359.0,34540.0
166.0,28750.0
112.0,25330.0
 71.2,31030.0
 28.1,14800.0
 18.5,12300.0
 17.9,11200.0
 13.7,10500.0
 10.0, 8090.0
  6.5, 8590.0
  6.1, 7280.0
  5.6, 5420.0
```

Sample Output for Determining the Effect of Temperature on Isotherms

```
COMPOUND = TCE
NUMBER OF DATA POINTS = 14
TEMPERATURE OF THE KNOWN ISOTHERM =     10.00 C
TEMPERATURE OF THE UNKNOWN ISOTHERN =     21.00 C
SOLUBILITY OF KNOWN ISOTHERM=   836.60 mg/L
SOLUBILITY OF UNKNOWN ISOTHERM=  1062.40 mg/L
MOLECULAR WEIGHT =    131.29
LIQIUD DENSITY =    1.4620 g/cm3


          ADSORPTION         HEAT OF
DATA      POTENTIAL         ADSORPTION
POINT     (cal/gmol)        (cal/gmol)

  1        4358.549            7949.6
  2        6699.681           10290.8
  3        4360.113            7951.2
  4        4793.850            8384.9
  5        5015.117            8606.2
  6        5269.852            8861.0
  7        5792.655            9383.8
  8        6027.705            9618.8
  9        6046.244            9637.3
 10        6196.612            9787.7
 11        6373.637            9964.7
 12        6615.875           10207.0
 13        6651.590           10242.7
 14        6699.681           10290.8


                 KNOWN                  PREDICTION
              AT  10.0 C                AT  21.0 C
DATA
POINT     C (ug/L)      Q (ug/g)         C (ug/L)

  1       360.000      39281.00         610.970
  2         5.600       6941.70          11.106
  3       359.000      34540.00         609.336
  4       166.000      28750.00         290.004
  5       112.000      25330.00         198.567
  6        71.200      31030.00         128.390
  7        28.100      14800.00          52.464
  8        18.500      12300.00          35.085
  9        17.900      11200.00          33.989
 10        13.700      10500.00          26.276
 11        10.000       8090.00          19.406
 12         6.500       8590.00          12.819
 13         6.100       7280.00          12.059
 14         5.600       5420.00          11.106
```

APPENDIX VIII. COMPUTER CODE FOR THE IDEAL ADSORBED SOLUTION THEORY MODEL

```
C
C                           IAST PREDICTION
C
C         THIS PROGRAM WILL PREDICT COMPETITIVE ADSORPTION EFFECTS
C     FOR A MULTICOMPONENT ISOTHERM GIVEN THE SINGLE SOLUTE ISOTHERM
C     PARAMETERS AND THE INITIAL CONCENTRATIONS OF THE COMPONENTS,
C     THE SYSTEM VOLUME, AND THE MASS OF CARBON.  THIS IS COMPLETED
C     BY SIMULTANEOUSLY SOLVING THE IDEAL ADSORBED SOLUTION THEORY
C     EQUATION USING A VARIATION OF THE NEWTON/RAPHSON METHOD
C     WHICH IS FOUND IN THE SUBROUTINE ZSPOW WHICH IS IN THE IMSL
C     LIBRARY ZERXTD.  IF THE MULTICOMPONENT DATA POINTS ARE ENTERED
C     IN THE INPUT FILE, THE PROGRAM WILL CALCULATE THE PERCENT
C     ERROR OF THE PREDICTED CONCENTRATIONS AND THE RELATIVE
C     PERCENTAGE ERROR FOR EACH COMPONENT.
C
C         THE IAS THEORY ASSUMES EQUAL SPREADING PRESSURE FOR EACH
C     COMPOUND AND THE TOTAL MIXTURE.  THE PROGRAM THEREFORE WILL
C     GIVE THE LIQUID CONCENTRATIONS THAT THE SINGLE SOLUTE
C     FREUNDLICH ISOTHERM PARAMETERS SHOULD BE EVALUATED AT TO
C     OBTAIN EQUAL SPREADING PRESSURES.  THIS IS LISTED FOR EACH
C     DOSAGE IN THE CHECKING CONCENTRATION RANGES SECTION
C     FOUND IN THE OUTPUT FILE.
C
C     PROGRAM WRITTEN BY:  THOMAS F. SPETH, PAUL LUFT, AND DR.
C                          JOHN CRITTENDEN
C
C
C     PROGRAM LANGUAGE:  FORTRAN-77
C
C
C                         VARIABLE LISTING
C
C     C      = LIQUID PHASE CONCENTRATIONS (ug/L)
C     CEX    = EXPERIMENTAL LIQUID PHASE CONCENTRATIONS (ug/L)
C     CI     = Clo OF THE PREDICTED DATA
C     CO     = INITIAL CONCENTRATIONS (ug/L)
C     ERRORC= RELATIVE PERCENTAGE ERROR BETWEEN CEXP AND C
C     ERRORQ= RELATIVE PERCENTAGE ERROR BETWEEN QEXP AND Q
C     FCN    = SUBROUTINE THAT SETS UP THE NON-LINEAR EQUATIONS
C     FNORM = OUTPUT: SUM OF THE SQUARES OF THE RESIDUALS AT X
C     HIGH   = HIGHEST CONCENTRATION IN SINGLE SOLUTE ISOTHERM (um/L)
C     I      = COUNTER
C     IER    = OUTPUT: ERROR PARAMETER
C     ITMAX = THE MAXIMUM NUMBER OF ITERATIONS
C     J      = COUNTER FOR EACH DOSAGE
C     JJ     = COUNTER
C     K      = FREUNDLICH ISOTHERM PARAMETER (um/g)(L/um)**1/n
C     L      = COUNTER FOR ADJUSTING ZZ WHEN ERROR IS PRESENT
C     LOW    = LOWEST CONCENTRATION IN SINGLE SOLUTE ISOTHERM (um/L)
C     M      = DOSAGE OF CARBON (mg)
C     MW     = MOLECULAR WEIGHTS
C     N      = NUMBER OF EQUATIONS TO BE SOLVED (NUMBER OF UNKNOWNS)
```

```
C      NC     = NUMBER OF COMPONENTS
C      ND     = NUMBER OF CARBON DOSAGES
C      NDC    = NUMBER OF CARBON DOSAGES (COUNTER)
C      NDQ    = NUMBER OF CARBON DOSAGES (COUNTER)
C      NSIG   = NUMBER OF DIGITS OF ACCURACY DESIRED IN COMPUTED ROOT
C      PAR    = PARAMETER SET
C      PAR(1 TO NC)= FREUNDLICH K VALUES
C      PAR(10 TO 10+NC)= FREUNDLICH N VALUES
C      PAR(20 TO 20+NC)= INITIAL CONCENTRATIONS
C      PAR(30)= CARBON DOSAGE
C      PAR(40)= VOLUME OF ISOTHERM BOTTLE
C      PEC   = PERCENTAGE ERROR BETWEEN CEXP AND C
C      PEQ   = PERCENTAGE ERROR BETWEEN QEXP AND Q
C      Q     = SOLID PHASE CONCENTRATION (ug/g): TWO DIMENSIONAL
C      QEX   = SOLID PHASE CONCENTRATION (ug/g): EXPERIMENTAL
C      QT    = TOTAL SURFACE LOADINGS (ug/g)
C      QNQ   = SUM OF Q*XN
C      RPEC  = SUM OF PEC
C      RPEQ  = SUM OF PEQ
C      V     = VOLUMES OF BOTTLES (L)
C      WK    = WORK VECTOR: LENGTH=N*(3*N+15)/2
C      X     = SOLID PHASE CONCENTRATION (ug/g) ONE DIMENSION
C      XN    = FREUNDLICH ISOHTERM PARAMETER 1/n
C      ZSPOW= SUBROUTINE THAT SOLVES THE NON-LINEAR EQUATIONS
C      ZZ    = VARIABLE USED TO CALCULATE INITIAL Q
C
C
C                      SAMPLE INPUT
C
C      NC,ND
C      M(1),V(1)
C      M(2),V(2)
C      ..   ..
C      M(ND),V(ND)
C      CHAR(1),K(1), XN(1), CO(1), MW(1)
C      LOW(1),HIGH(1)
C      CEX(1,1),QEX(1,1)
C      CEX(1,2),QEX(1,2)
C      ...       ...
C      CEX(1,ND),QEX(1,ND)
C      CHAR(2), K(2), XN(2), CO(2), MW(2)
C      LOW(2),HIGH(2)
C      CEX(2,1),QEX(2,1)
C      CEX(2,2),QEX(2,2)
C      ...       ...
C      CEX(2,ND),QEX(2,ND)
C      ETC.,ETC.,,,,,,,,
C      ETC.,ETC.,,,,,,,,
C      CHAR(NC),K(NC),XN(NC),CO(NC),MW(NC)
C      LOW(NC),HIGH(NC)
C      CEX(NC,1),CEX(NC,1)
C      CEX(NC,2),CEX(NC,2)
C      ...        ...
C      CEX(NC,ND),QEX(NC,ND)
C
```

```
C
C     *********************PROGRAM*********************
C
C
C                      DIMENSIONING
C
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION XN(10),CO(10),Q(10,50),V(50),PAR(50),X(10),
     $C(10,50),WK(200),HIGH(10),CI(10,50),CEX(10,50),QEX(10,50),
     $PEC(10,50),PEQ(10,50),ERRORC(10),ERRORQ(10)
      CHARACTER*10 CHAR(10)
      DOUBLE PRECISION M(50),MW(10),K(10),LOW(10)
      EXTERNAL FCN
C
C                    READ CONSTANTS
C
      OPEN(4,FILE='IAST.DAT')
      OPEN(7,FILE='IAST.OUT')
      PRINT*, 'READING INPUT'
      READ(4,*) NC,ND
      DO 10 I=1,ND
       READ(4,*) M(I),V(I)
       M(I)=M(I)/1000.0D0
10    CONTINUE
      DO 20 I=1,NC
       READ(4,*) CHAR(I),K(I),XN(I),CO(I),MW(I)
       READ(4,*) LOW(I),HIGH(I)
       READ(4,*) CEX(I,1),QEX(I,1)
       IF (CEX(I,1) .EQ. 0.0D0 .AND. QEX(I,1) .EQ. 0.0D0) THEN
        DO 14 J=2,ND
         CEX(I,J)=0.0D0
         QEX(I,J)=0.0D0
14      CONTINUE
       ELSE
        DO 15 J=2,ND
         READ(4,*) CEX(I,J),QEX(I,J)
15      CONTINUE
       ENDIF
       CO(I)=CO(I)/MW(I)
       XN(I)=1.0D0/XN(I)
20    CONTINUE
      WRITE(7,21)
21    FORMAT(1X,' ')
C
C                  SOLVE EACH DOSAGE INDIVIDUALLY
C
      PRINT*, 'SOLVING EACH DOSAGE'
      DO 100 J=1,ND
       L=0
       ZZ=0.50D0
C
C                 CALCULATE INITIAL QUESSES ON Q'S
C
25     IF (J .EQ. 1) THEN
        DO 30 I=1,NC
```

```
         Q(I,1)=ZZ*CO(I)*V(1)/M(1)
30      CONTINUE
       ELSE
        DO 40 I=1,NC
         Q(I,J)=ZZ*Q(I,J-1)
40      CONTINUE
       ENDIF
C
C                  PUT Q INTO ONE DIMENSIONAL FORM
C
       DO 45 I=1,NC
        X(I)=Q(I,J)
45     CONTINUE
C
C                   ENTER THE PARAMETERS FOR ZSPOW
C
       DO 50 I=1,NC
        PAR(I)=K(I)
        PAR(10+I)=XN(I)
        PAR(20+I)=CO(I)
50     CONTINUE
       PAR(30)=M(J)
       PAR(40)=V(J)
       NSIG=4
52     N=NC
       ITMAX=100
C
C                  CALL ZSPOW TO SOLVE EQUATIONS
C
       CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
C
C                         FIX ANY ERROR
C
       IF (IER .EQ. 129 .OR. IER .EQ. 131) THEN
        IF (L .EQ. 0) THEN
         ZZ=0.9D0
         L=L+1
         GOTO 25
        ENDIF
        IF (L .EQ. 1) THEN
         ZZ=0.1D0
         L=L+1
         GOTO 25
        ENDIF
        IF (L .EQ. 2) THEN
         WRITE(7,55) M(J)*1000.0D0
55       FORMAT(1X,'THERE IS A PROBLEM WITH THE INITIAL CONCENTRATIONS',
     $/,'THAT THE PROGRAMS FIXING ROUTINE DID NOT HELP.  DOSAGE=',F10.4)
        ENDIF
       ENDIF
C
       IF (IER .EQ. 130) THEN
        NSIG=NSIG-1
        IF (NSIG .LT. 0) THEN
         WRITE(7,57) M(J)*1000.0D0
```

```
57       FORMAT(1X,'THE NUMBER OF SIGNIFICANT FIGURES HAS DROPPED ',/,
     $1X,'BELOW ZERO.  THERE ARE NO RESULTS FOR DOSAGE= ',F10.4)
         GOTO 100
        ENDIF
        GOTO 52
       ENDIF
C
C            SET X TO TWO DIMENSIONAL FORM FOR PRINT OUT
C
       DO 58 I=1,NC
        Q(I,J)=X(I)
58     CONTINUE
C
C               CALCULATE THE LIQUID CONCENTRATION
C
       DO 60 I=1,NC
        C(I,J)=CO(I)-M(J)/V(J)*Q(I,J)
60     CONTINUE
C
C                         CALCULATE Cio
C
       CISUM=0.0D0
       DO 64 I=1,NC
        CISUM=CISUM+XN(I)*Q(I,J)
64     CONTINUE
       DO 66 I=1,NC
        CI(I,J)=(CISUM/XN(I)/K(I))**XN(I)
66     CONTINUE
C
C                       PUT INTO ug/L UNITS
C
       DO 70 I=1,NC
        Q(I,J)=Q(I,J)*MW(I)
        C(I,J)=C(I,J)*MW(I)
70     CONTINUE
100   CONTINUE
C
C                   CALCULATE THE PERCENTAGE ERROR
C
      DO 140 I=1,NC
       RPEC=0.0D0
       RPEQ=0.0D0
       NDC=ND
       NDQ=ND
       DO 130 J=1,ND
        PRINT*, 'CEX(I,J)= ',CEX(I,J),' QEX(I,J)= ',QEX(I,J)
        IF (CEX(I,J) .EQ. 0.0D0) THEN
         NDC=NDC-1
         PEC(I,J)=(CEX(I,J)-C(I,J))/CEX(I,J)*100.0D0
        ELSE
         PEC(I,J)=(CEX(I,J)-C(I,J))/CEX(I,J)*100.0D0
         RPEC=RPEC+DABS(PEC(I,J))
        ENDIF
        IF (QEX(I,J) .EQ. 0.0D0) THEN
         NDQ=NDQ-1
         PEQ(I,J)=(QEX(I,J)-Q(I,J))/QEX(I,J)*100.0D0
        ELSE
         PEQ(I,J)=(QEX(I,J)-Q(I,J))/QEX(I,J)*100.0D0
         RPEQ=RPEQ+DABS(PEQ(I,J))
        ENDIF
130    CONTINUE
       ERRORC(I)=RPEC/NDC
       ERRORQ(I)=RPEQ/NDQ
140   CONTINUE
C
C                           PRINT OUT
C
      PRINT*, 'PRINTING OUTPUT'
      WRITE(7,200)
200   FORMAT(//,8X,'FREUNDLICH PARAMETERS',/)
      IF (MW(1) .EQ. 1.0D0) THEN
       WRITE(7,209)
209    FORMAT(/,'COMPONENT',T15,'K (um/g)(L/um)**1/n',T38,'1/n',T45,
     $ 'CO (um/L)',/)
      ELSE
       WRITE(7,210)
210    FORMAT(/,'COMPONENT',T15,'K (ug/g)(L/ug)**1/n',T38,'1/n',T45,
     $ 'CO (ug/L)',/)
      ENDIF
      DO 300 I=1,NC
       WRITE(7,220) CHAR(I),K(I),1/XN(I),CO(I)*MW(I)
220    FORMAT(1X,A10,T20,F8.3,T35,F7.4,T44,F9.4,/)
300   CONTINUE
      WRITE(7,310)
310   FORMAT(//,5X,'IAST PREDICTION AND COMPARISON')
      WRITE(7,320) CHAR(1),CHAR(2),CHAR(3)
320   FORMAT(///,1X,'DOSAGE',T15,A10,T37,A10,T60,A10)
      IF (MW(1) .EQ. 1.0D0) WRITE(7,329)
329   FORMAT(/,2X,'(mg)',T14,'C um/L',T24,'Q um/g',T35,'C um/L',T45,
     $'Q um/g',T56,'C um/L',T66,'Q um/g',/)
      IF (MW(1) .NE. 1.0D0) WRITE(7,330)
330   FORMAT(/,2X,'(mg)',T14,'C ug/L',T24,'Q ug/g',T35,'C ug/L',T45,
     $'Q ug/g',T56,'C ug/L',T66,'Q um/g',/)
      DO 340 J=1,ND
       M(J)=M(J)*1000.0D0
       WRITE(7,360) M(J),C(1,J),Q(1,J),C(2,J),Q(2,J),C(3,J),Q(3,J)
       WRITE(7,361) PEC(1,J),PEQ(1,J),PEC(2,J),PEQ(2,J),PEC(3,J),
     $ PEQ(3,J)
340   CONTINUE
      IF (NC .GT. 3) THEN
       WRITE(7,320) CHAR(4),CHAR(5),CHAR(6)
       IF (MW(1) .EQ. 1.0D0) WRITE(7,329)
       IF (MW(1) .NE. 1.0D0) WRITE(7,330)
       DO 350 J=1,ND
        WRITE(7,360) M(J),C(4,J),Q(4,J),C(5,J),Q(5,J),C(6,J),Q(6,J)
        WRITE(7,361) PEC(4,J),PEQ(4,J),PEC(5,J),PEQ(5,J),PEC(6,J),
     $  PEQ(6,J)
350    CONTINUE
      ENDIF
      IF (NC .GT. 6) THEN
```

```
       WRITE(7,320) CHAR(7),CHAR(8),CHAR(9)
       IF (MW(1) .EQ. 1.0D0) WRITE(7,329)
       IF (MW(1) .NE. 1.0D0) WRITE(7,330)
       DO 355 J=1,ND
        WRITE(7,360) M(J),C(7,J),Q(7,J),C(8,J),Q(8,J),C(9,J),Q(9,J)
        WRITE(7,361) PEC(7,J),PEQ(7,J),PEC(8,J),PEQ(8,J),PEC(9,J),
     $ PEQ(9,J)
355    CONTINUE
      ENDIF
360   FORMAT(F6.2,T10,F10.5,T21,F10.3,T32,F10.5,T43,F9.3,T53,F10.5
     $,T64,F9.3)
361   FORMAT('% ERROR',T12,F8.3,T22,F8.3,T34,F8.3,T44,F8.3,T55,F8.3,
     $T65,F8.3,/)
      DO 380 I=1,NC
       IF (CEX(I,1) .EQ. 0.0D0 .AND. QEX(I,1) .EQ. 0.0D0) GOTO 380
       WRITE(7,370) CHAR(I),ERRORC(I),CHAR(I),ERRORQ(I)
370    FORMAT(/,1X,'RELATIVE PERCENTAGE ERROR IN C FOR ',A10,'=',F8.3,
     $ /,1X,'RELATIVE PERCENTAGE ERROR IN Q FOR ',A10,'=',F8.3)
380   CONTINUE
      WRITE(7,400)
400   FORMAT(///,T20,'CHECKING CONCENTRATION RANGES OF S.S. ISOTHERM')
      WRITE(7,410) CHAR(1),CHAR(2),CHAR(3),CHAR(4),CHAR(5)
410   FORMAT(//,1X,'DOSAGE',T15,A10,T26,A10,T37,A10,T48,A10,T59,A10,/,
     $1X,T15,'um/L',T26,'um/L',T37,'um/L',T48,'um/L',T59,'um/L',/)
      WRITE(7,420) LOW(1),LOW(2),LOW(3),LOW(4),LOW(5)
420   FORMAT(1X,'S.S. LOW',T12,F9.4,T22,F9.4,T33,F9.4,T44,F9.4,T56,F9.4)
      WRITE(7,430) HIGH(1),HIGH(2),HIGH(3),HIGH(4),HIGH(5)
430   FORMAT(1X,'S.S. HIGH',T12,F9.4,T22,F9.4,T33,F9.4,T44,F9.4,T56,
     $F9.4,/)
      DO 450 J=1,ND
       WRITE(7,440) M(J),CI(1,J),CI(2,J),CI(3,J),CI(4,J),CI(5,J)
440    FORMAT(1X,F6.2,T12,F10.6,T22,F10.6,T33,F10.6,T44,F10.6,T56,F10.6)
450   CONTINUE
      IF (NC .GT. 5) THEN
       WRITE(7,410) CHAR(6),CHAR(7),CHAR(8),CHAR(9),CHAR(10)
       WRITE(7,420) LOW(6),LOW(7),LOW(8),LOW(9),LOW(10)
       WRITE(7,430) HIGH(6),HIGH(7),HIGH(8),HIGH(9),HIGH(10)
       DO 460 J=1,ND
        WRITE(7,440) M(J),CI(6,J),CI(7,J),CI(8,J),CI(9,J),CI(10,J)
460    CONTINUE
      ENDIF
      WRITE(7,900)
900   FORMAT(/,1X,'S.S. REFERS TO THE SINGLE SOLUTE ISOTHERM WHICH WAS',
     $/,'USED TO FIND THE FREUNDLICH PARAMETERS.  LISTED ARE THE HIGH',/
     $,'AND LOW LIQIUD CONCENTRATIONS.')
1000  STOP
      END
C
C
C                   SUBROUTINE FCN
C
C     THIS SUBROUTINE WILL SET UP THE EQUATIONS THAT WILL BE USED IN
C     THE ZSPOW SUBROUTINE
C
      SUBROUTINE FCN(X,F,N,PAR)
```

```
C
      DOUBLE PRECISION X(N),F(N),PAR(50),QNQ,QT
      INTEGER I,N
      QT=0.0D0
      QNQ=0.0D0
      DO 1010 I=1,N
       QT=QT+X(I)
       QNQ=QNQ+PAR(10+I)*X(I)
1010  CONTINUE
      DO 1020 I=1,N
       F(I)=PAR(20+I)-PAR(30)/PAR(40)*X(I)-X(I)/QT*(QNQ/PAR(10+I)/
     $ PAR(I))**PAR(10+I)
1020  CONTINUE
      RETURN
      END
```

Sample Input - Ideal Adsorbed Solution Theory

```
7,15
2.11,.160
6.11,.160
8.17,.160
9.98,.160
11.83,.160
15.61,.160
17.45,.160
19.99,.160
24.57,.160
25.83,.160
28.00,.160
32.29,.160
36.02,.160
40.20,.160
47.22,.160
'DCE',46.9,.5562,1170.0,96.94
0.117,55.5
1110.0,4550.0
1110.0,1570.0
996.0,3410.0
719.0,7230.0
703.0,6320.0
592.0,5930.0
515.0,6010.0
440.0,5840.0
354.0,5320.0
343.0,5120.0
293.0,5010.0
239.0,4620.0
200.0,4310.0
165.0,4000.0
143.0,3480.0
'TCE',191.7,.4328,120.0,131.29
0.0427,2.7420
0.0,0.0
'PCE',650.6,.4579,80.0,165.83
0.161,47.2
0.0,0.0
'TOL',475.1,.3282,100.0,92.15
0.06,37.5
0.0,0.0
'EB',714.4,.2953,13.0,106.17
0.04,26.6
0.0,0.0
'OP-XYL',894.6,.2587,29.5,106.17
0.36,35.7
0.0,0.0
'M-XYL',1044.0,.2458,20.8,106.17
0.5,41.3
0.0,0.0
```

Sample Output - Ideal Adsorbed Solution Theory

```
          FRUENDLICH PARAMETERS

COMPONENT      K (um/g)(L/um)**1/n     1/n     CO (ug/L)

 DCE                   46.900        0.5562   1170.0000

 TCE                  191.700        0.4328    120.0000

 PCE                  650.600        0.4579     80.0000

 TOL                  475.100        0.3282    100.0000

 EB                   714.400        0.2953     13.0000

 OP-XYL               894.600        0.2587     29.5000

 M-XYL               1044.000        0.2458     20.8000


        IAST PREDICTION AND COMPARISON


 DOSAGE      DCE                      TCE                      PCE

  (mg)     C ug/L       Q ug/g      C ug/L     Q   ug/g      C ug/L     Q ug/g

  2.11   1085.63898   6397.044    54.18856   4990.441     4.59701   5717.763
 % ERROR      2.195    -40.594    --------   --------    --------   --------

  6.11    826.62054   8991.934    12.30677   2820.117     0.72213   2076.016
 % ERROR     25.530   -472.735    --------   --------    --------   --------

  8.17    710.25962   9003.483     7.63140   2200.609     0.43895   1558.111
 % ERROR     28.689   -164.032    --------   --------    --------   --------

  9.98    622.87188   8771.593     5.42639   1836.851     0.31081   1277.582
 % ERROR     13.370    -21.322    --------   --------    --------   --------

 11.83    546.64326   8430.860     4.02731   1568.523     0.23092   1078.872
 % ERROR     22.241    -33.400    --------   --------    --------   --------

 15.61    424.59216   7640.311     2.43073   1205.066     0.14063    818.546
 % ERROR     28.278    -28.842    --------   --------    --------   --------

 17.45    378.17267   7260.308     1.97031   1082.221     0.11465    732.473
 % ERROR     26.568    -20.804    --------   --------    --------   --------

 19.99    324.79500   6765.023     1.51648    948.342     0.08899    639.608
 % ERROR     26.183    -15.839    --------   --------    --------   --------
```

24.57	252.15541	5977.010	1.00709	774.883	0.06001	520.570
% ERROR	28.770	-12.350	--------	--------	--------	--------
25.83	236.24209	5784.021	0.91005	737.685	0.05445	495.211
% ERROR	31.125	-12.969	--------	--------	--------	--------
28.00	212.03510	5474.085	0.77156	681.305	0.04649	456.877
% ERROR	27.633	-9.263	--------	--------	--------	--------
32.29	173.69984	4936.761	0.57363	591.769	0.03502	396.234
% ERROR	27.322	-6.856	--------	--------	--------	--------
36.02	148.08010	4539.344	0.45522	531.015	0.02809	355.233
% ERROR	25.960	-5.321	--------	--------	--------	--------
40.20	125.49837	4157.220	0.36003	476.179	0.02246	318.319
% ERROR	23.940	-3.931	--------	--------	--------	--------
47.22	97.65425	3633.531	0.24956	405.762	0.01610	271.017
% ERROR	31.710	-4.412	--------	--------	--------	--------

DOSAGE	TOL		EB		OP-XYL	
(mg)	C ug/L	Q ug/g	C ug/L	Q ug/g	C ug/L	Q ug/g
2.11	3.02464	7353.582	0.05537	981.583	0.01747	2235.642
% ERROR	--------	--------	--------	--------	--------	--------
6.11	0.28113	2611.296	0.00412	340.318	0.00098	772.478
% ERROR	--------	--------	--------	--------	--------	--------
8.17	0.14981	1955.450	0.00209	254.549	0.00046	577.714
% ERROR	--------	--------	--------	--------	--------	--------
9.98	0.09657	1601.658	0.00130	208.396	0.00027	472.942
% ERROR	--------	--------	--------	--------	--------	--------
11.83	0.06599	1351.601	0.00086	175.813	0.00017	398.983
% ERROR	--------	--------	--------	--------	--------	--------
15.61	0.03468	1024.629	0.00042	133.244	0.00008	302.369
% ERROR	--------	--------	--------	--------	--------	--------
17.45	0.02652	916.662	0.00032	119.195	0.00006	270.487
% ERROR	--------	--------	--------	--------	--------	--------
19.99	0.01898	800.248	0.00022	104.050	0.00004	236.118
% ERROR	--------	--------	--------	--------	--------	--------
24.57	0.01122	651.128	0.00012	84.655	0.00002	192.104
% ERROR	--------	--------	--------	--------	--------	--------

25.83	0.00985	619.374	0.00011	80.526	0.00002	182.733
% ERROR	--------	--------	--------	--------	--------	--------
28.00	0.00796	571.383	0.00008	74.285	0.00001	168.571
% ERROR	--------	--------	--------	--------	--------	--------
32.29	0.00542	495.483	0.00006	64.416	0.00001	146.175
% ERROR	--------	--------	--------	--------	--------	--------
36.02	0.00400	444.180	0.00004	57.746	0.00001	131.038
% ERROR	--------	--------	--------	--------	--------	--------
40.20	0.00297	397.998	0.00003	51.741	0.00000	117.413
% ERROR	--------	--------	--------	--------	--------	--------
47.22	0.00197	338.833	0.00002	44.049	0.00000	99.958
% ERROR	--------	--------	--------	--------	++++++++	--------

DOSAGE	M-XYL					
(mg)	C ug/L	Q ug/g	C ug/L	Q ug/g	C ug/L	Q ug/g
2.11	0.00386	1576.958	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
6.11	0.00019	544.676	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
8.17	0.00009	407.342	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
9.98	0.00005	333.466	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
11.83	0.00003	281.318	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
15.61	0.00001	213.197	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
17.45	0.00001	190.716	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
19.99	0.00001	166.483	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
24.57	0.00000	135.450	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000
25.83	0.00000	128.842	0.00000	0.000	0.00000	0.000
% ERROR	--------	--------	0.000	0.000	0.000	0.000

```
   28.00     0.00000   118.857    0.00000     0.000   0.00000     0.000
 % ERROR     --------  --------     0.000     0.000     0.000     0.000

   32.29     0.00000   103.066    0.00000     0.000   0.00000     0.000
 % ERROR     --------  --------     0.000     0.000     0.000     0.000

   36.02     0.00000    92.393    0.00000     0.000   0.00000     0.000
 % ERROR     --------  --------     0.000     0.000     0.000     0.000

   40.20     0.00000    82.786    0.00000     0.000   0.00000     0.000
 % ERROR     --------  --------     0.000     0.000     0.000     0.000

   47.22     0.00000    70.479    0.00000     0.000   0.00000     0.000
 % ERROR     ++++++++  --------     0.000     0.000     0.000     0.000

RELATIVE PERCENTAGE ERROR IN C FOR DCE        =  24.634
RELATIVE PERCENTAGE ERROR IN Q FOR DCE        =  56.845


                 CHECKING CONCENTRATION RANGES

DOSAGE        DCE        TCE        PCE        TOL        EB
              um/L       um/L       um/L       um/L       um/L

S.S. LOW      0.1170     0.0427     0.1610     0.0600     0.0400
S.S. HIGH    55.5000     2.7420    47.2000    37.5000    26.6000

   2.11     44.707617  2.860517   0.211799   0.108355   0.014861
   6.11     15.692829  0.744948   0.059379   0.018378   0.002068
   8.17     11.985334  0.526867   0.042801   0.011640   0.001245
   9.98      9.878857  0.410983   0.033845   0.008388   0.000865
  11.83      8.309284  0.329045   0.027429   0.006257   0.000625
  15.61      6.121864  0.222201   0.018926   0.003728   0.000351
  17.45      5.363419  0.187468   0.016117   0.002979   0.000274
  19.99      4.528496  0.150829   0.013123   0.002237   0.000199
  24.57      3.444467  0.106114   0.009412   0.001407   0.000119
  25.83      3.213824  0.097071   0.008652   0.001251   0.000104
  28.00      2.867144  0.083827   0.007532   0.001031   0.000084
  32.29      2.327623  0.064126   0.005847   0.000724   0.000057
  36.02      1.973006  0.051854   0.004783   0.000547   0.000042
  40.20      1.664047  0.041661   0.003889   0.000410   0.000030
  47.22      1.287526  0.029961   0.002848   0.000265   0.000019

DOSAGE        OP-XYL     M-XYL
              um/L       um/L       um/L       um/L       um/L

S.S. LOW      0.3600     0.5000     0.0000     0.0000     0.0000
S.S. HIGH    35.7000    41.3000     0.0000     0.0000     0.0000

   2.11      0.002059  0.000645   0.000000   0.000000   0.000000
```

6.11	0.000217	0.000060	0.000000	0.000000	0.000000
8.17	0.000121	0.000033	0.000000	0.000000	0.000000
9.98	0.000080	0.000021	0.000000	0.000000	0.000000
11.83	0.000055	0.000014	0.000000	0.000000	0.000000
15.61	0.000029	0.000007	0.000000	0.000000	0.000000
17.45	0.000022	0.000005	0.000000	0.000000	0.000000
19.99	0.000015	0.000004	0.000000	0.000000	0.000000
24.57	0.000008	0.000002	0.000000	0.000000	0.000000
25.83	0.000007	0.000002	0.000000	0.000000	0.000000
28.00	0.000006	0.000001	0.000000	0.000000	0.000000
32.29	0.000004	0.000001	0.000000	0.000000	0.000000
36.02	0.000003	0.000001	0.000000	0.000000	0.000000
40.20	0.000002	0.000000	0.000000	0.000000	0.000000
47.22	0.000001	0.000000	0.000000	0.000000	0.000000

S.S. REFERS TO THE SINGLE SOLUTE ISOTHERM WHICH WAS USED TO FIND THE FREUNDLICH PARAMETERS. LISTED ARE THE HIGH AND LOW LIQUID CONCENTRATIONS.

APPENDIX IX. COMPUTER CODE FOR THE HYPOTHETICAL COMPONENTS MODEL

```
C
C
C          ******HYPOTHETICAL COMPONENT PROGRAM*******
C
C       THIS PROGRAM WILL FIT A TRACER ISOTHERM TO DETERMINE
C     ONE TO SIX HYPOTHETICAL COMPONENTS.  THE MULTICOMPETITIVE EFFECTS
C     ARE CALCULATED USING IDEAL ADSORBED SOLUTION THEORY.  THE PROGRAM
C     USES IMSL ROUTINES, THEREFORE, IT WILL NEED TO BE COMPILED IN IBM
C     PROFESSIONAL FORTRAN.  IMSL LIBRARY ZERXTD MUST BE USED.  THIS
C     LIBRARY CONTAINS BOTH ZSPOW AND ZXSSQ.
C
C       SINCE THERE ARE THREE FREUNDLICH PARAMETERS FOR EACH HYPOTHETICAL
C     COMPONENT, THERE IS A MAXIMUM OF 18 PARAMETERS THAT CAN BE USED.
C     THIS PROGRAM WILL LET YOU DECIDE WHICH OF THE FREUNDLICH PARAMETERS
C     WILL BE VARIED BY THE PROGRAM.  IT IS SUGGESTED THAT YOU DO NOT
C     VARY ALL 18 PARAMETERS BECAUSE THE PROGRAM WILL RUN VERY SLOWLY.
C
C     THE PROGRAM REQUIRES THE FREUNDLICH PARAMETERS AND INITIAL
C     CONCENTRATION OF THE TRACER COMPOUND, AND THE DOSAGES, BOTTLE
C     VOLUMES, AND LIQUID PHASE CONCENTRATIONS FOR THE TRACER
C     ISOTHERM.  ALSOREQUIREDARE THE INITIAL GUESSESOF THE FREUNDLICH
C     PARAMETERS FOR THE HYPOTHETICAL COMPONENTS.  THE OUTPUT WILL
C     CONTAIN THE INPUT PARAMETERS AND THE FINAL FREUNDLICH
C     PARAMETERS FOR THE HYPOTHETICAL COMPONENTS.  THE LIQUID
C     AND SOLID PHASE CONCENTRATIONS FOR THE TRACER AND THE
C     HYPOTHETICAL COMPONENTS FOR EACH DOSAGE ARE ALSO LISTED
C     AS IS VARIOUS STATISTICAL PARAMETERS.
C
C       THE RESIDUALS CAN BE CALCULATED TWO WAYS.  ONE WAY IS TO USE
C     THE CHANGE IN THE LIQUID CONCENTRATIONS ARE THE RESIDUAL (RES=0),
C     AND THE OTHER IS TO USE THE NORMALIZED CHANGE IN THE LIQIUD
C     CONCENTRATIONS AS THE RESIDUAL (RES=1).
C
C     PROGRAM WRITTEN BY:  THOMAS FRANCIS SPETH
C
C     SPECIAL THANKS TO: PAUL LUFT, AND DR. JOHN CRITTENDEN FOR THEIR
C     PREVIOUS WORK.
C
C               ***VARIABLE DEFINITIONS***
C
C      AA    = 0(NO), 1(YES) - IS PREVIOUS PARAMETER IS TO BE VARIED?
C      CE    = RAW EQUILIBRIUM CONCENTRATIONS FOR KNOWN COMPONENT (ug/L)
C      CHAR  = NAME OF THE KNOWN COMPOUND
C      CI    = EQUILIBRIUM LIQUID CONCENTRATIONS FROM IAST
C      CO    = INITIAL CONCENTRATION OF KNOWN COMPONENT (ug/L)
C      D     = NUMBER OF BOTTLE POINTS
C      DM    = DOSAGES OF CARBON (mg)
C      DELTA = THIRD CONVERGENCE CRITERIA (SET TO ZERO)
C      EPS   = SECOND CONVERGENCE CRITERIA (SUM OF THE SQUARES OF THE
C              RESIDUALS:  CAN BE SET TO ZERO)
C      F     = OUTPUT CONTAINING RESIDUALS
C      HC    = NAME OF HYPOTHETICAL COMPONENT
C      IAST  = SUBROUTINE THAT CALCULATES RESIDUALS OF CE (IAST PROGRAM)
```

```
C     IER   = ERROR PARAMETER
C     INFER = INDICATES WHICH CONVERGENCE CRITERIA WAS SATISFIED
C     IOPT  = INPUT OPTIONS PARAMETER (0,1,or 2:  SEE MANUAL)
C     IXJAC = INPUT ROW DIMENSION OF MATRIX XJAC
C     J     = COUNTER
C     K     = FREUNDLICH ISOTHERM PARAMETER (um/g)*(L/um)**1/n  TRACER
C     M     = NUMBER OF ORIGINALS OR OBSERVATIONS
C     MAXFN = MAXIMUM NUMBER OF FUNCTION EVALUATIONS
C     MW    = MOLECULAR WEIGHT OF KNOWN COMPONENT
C     MWHC  = MOLECULAR WEIGHTS OF THE HYPOTHETICAL COMPONENTS
C     NA    = NUMBER OF UNKNOWN PARAMETERS
C     NN    = NUMBER OF HYPOTHETICAL COMPONENTS
C     NSIG  = FIRST CONVERGENCE CRITERIA (NUMBER OF SIGNIFICANT DIGITS)
C     P     = INITIAL PARAMETER GUESSES FOR H.C.'S
C     PARM  = INPUT VECTOR (ONLY USED WHEN IOPT=2)
C     PD    = PERCENT DIFFERENCE BETWEEN CE(EXP) AND CI(IAST)
C     QI    = SOLID CONCENTRATION (ug/g)
C     RES   = COUNTER TO DETERMINE WHICH RESIDUAL IS TO BE USED
C     SSQ   = RESIDUALS SUM OF SQUARES
C     V     = VOLUMES OF BOTTLES (L)
C     WORK  = WORK VECTOR (USED ONLY WHEN IOPT=2)
C     X     = PARAMETER VALUES
C     XJAC  = OUTPUT CONTAINING JACOBIAN
C     XJTJ  = OUTPUT (XJAC-TRANSPOSED)
C     XN    = FRUENDLICH ISOTHERM PARAMETER 1/n  TRACER
C     ZXSSQ = SUBROUTINE USED TO FIT THE DATA
C
C
C                    ***INPUT***
C
C     CHAR,D,K,XN,CO,MW
C     DM(1),V(1),CE(1)
C     DM(2),V(2),CE(2)
C     ..     ..     ..
C     DM(D),V(D),CE(D)
C     NN
C     HC1,K(HYP1),AA(1), 1/N(HYP1),AA(2), CO(HYP1),AA(3), MWHC(HYP1)
C     (THE FOLLOWING ARE USED IF NEEDED.)
C     HC2,K(HYP2),AA(4), 1/N(HYP2),AA(5), CO(HYP2),AA(6), MWHC(HYP2)
C     HC3,K(HYP3),AA(7), 1/N(HYP3),AA(8), CO(HYP3),AA(9), MWHC(HYP3)
C     HC4,K(HYP4),AA(10),1/N(HYP4),AA(11),CO(HYP4),AA(12),MWHC(HYP4)
C     HC5,K(HYP5),AA(13),1/N(HYP5),AA(14),CO(HYP5),AA(15),MWHC(HYP5)
C     HC6,K(HYP6),AA(16),1/N(HYP5),AA(17),CO(HYP6),AA(18),MWHC(HYP6)
C     RES
C     NSIG, EPS, DELTA, IOPT
C
C     WHERE, (HYP) REFERS TO THE ORIGINAL GUESSES OF THE FRUENDLICH
C     CONSTANTS FOR THE HYPOTHETICAL COMPONENTS. THE UNITS OF THE
C     HYPOTHETICAL COMPONENTS ARE:  (um/ug)(L/um)**1/n FOR K(HYP),
C     AND (ug/L) FOR CO(HYP).  IF YOU WISH TO INPUT CO(HYP) IN
C     UNITS OF (um/L), ENTER 1.0 FOR ITS MOLECULAR WEIGHT.
C
C        HYPOTHETICAL COMPONENTS TWO THROUGH SIX MAY OR MAY NOT
C     BE NEEDED.
C
```

```
C        THE VARIABLES AA(1) THROUGH AA(16) ARE INTEGERS USED TO
C     DETERMINE WHICH PARAMETERS ARE TO BE VARIED.  IF IT IS 1 THE
C     PREVIOUS PARAMETER IS TO BE VARIED.  IF IT IS 0 THE PREVIOUS
C     PARAMETER IS NOT TO BE VARIED.  FOR EXAMPLE, IF AA(3) IS 1, THE
C     PARAMETER CO(HYP1) IS TO BE VARIED IN THE PROGRAM.
C
C        IF A REASONABLY SMALL NSIG IS BEING USED, EPS CAN BE SET TO
C     ZERO.  THE PROGRAM WILL FINISH WHEN EITHER OF THE CONVERGENCE
C     CRITERIA IS SATISFIED.  IOPT SHOULD BE SET TO ZERO.  IF THE
C     RUN FAILS, WHICH IT SHOULDN'T, THEN CONSIDERATION SHOULD BE
C     MADE TO WHETHER IOPT SHOULD BE CHANGED.  CHANGING IOPT TO
C     1 IS RECOMMENDED IF IOPT IS TO BE CHANGED.  IF 2 IS CHOSEN,
C     PARM(1 -4) ARE TO BE INSERTED, IN ORDER, ON THE FOLLOWING
C     LINE.
C
C     DELTA SHOULD/CAN BE SET TO ZERO.
C
C              *********PROGRAM*********
C
C                   ***DIMENSIONS***
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      EXTERNAL IAST
      DOUBLE PRECISION MW,K,MWHC
      DIMENSION PARM(4),X(18),F(50),XJAC(50,18),XJTJ(171),WORK(361),
     $CE(50),PD(50),CI(7,50),V(50),QI(7,50),MWHC(6),P(18),B(18),DM(50)
      CHARACTER*10 CHAR,HC(6)
      CHARACTER*1 SR(18)
      INTEGER D,RES,AA(18)
      COMMON /ZSQ/ DM,CO,V,K,XN,D,CE,NN,RES,MW,P,AA,B,CI,QI,NC
C
C                  ***OPEN FILES***
C
      OPEN(UNIT=4,FILE='HC.DAT')
      OPEN(UNIT=7,FILE='HC.OUT')
C
C                 ***READ DATA***
C
      PRINT*, 'READING DATA'
      READ(4,*) CHAR,D,K,XN,CO,MW
      XN=1.0D0/XN
      CO=CO/MW
      DO 10 I=1,D
       READ(4,*) DM(I),V(I),CE(I)
       DM(I)=DM(I)/1000.0D0
       CE(I)=CE(I)/MW
10    CONTINUE
C
C            ***READ INITIAL PARAMETER GUESSES***
C
      READ(4,*) NN
      READ(4,*) HC(1),P(1),AA(1),P(2),AA(2),P(3),AA(3),MWHC(1)
      IF (NN .GE. 2) READ(4,*) HC(2),P(4),AA(4),P(5),AA(5),P(6),
     $AA(6),MWHC(2)
      IF (NN .GE. 3) READ(4,*) HC(3),P(7),AA(7),P(8),AA(8),P(9),
     $AA(9),MWHC(3)
      IF (NN .GE. 4) READ(4,*) HC(4),P(10),AA(10),P(11),AA(11),
     $P(12),AA(12),MWHC(4)
      IF (NN .GE. 5) READ(4,*) HC(5),P(13),AA(13),P(14),AA(14),
     $P(15),AA(15),MWHC(5)
      IF (NN .EQ. 6) READ(4,*) HC(6),P(16),AA(16),P(17),AA(17),
     $P(18),AA(18),MWHC(6)
      READ(4,*) RES
      READ(4,*) NSIG,EPS,DELTA,IOPT
      IF (IOPT .EQ. 2) THEN
       READ(4,*) PARM(1),PARM(2),PARM(3),PARM(4)
      ENDIF
C
C              ***WRITE INITIAL PARAMETER GUESSES***
C
      WRITE(7,15)
15    FORMAT(10X,'INITIAL H.C. GUESSES',//)
      WRITE(7,18)
18    FORMAT(1X,'COMPONENT',T15,'K (um/g)(L/um)**1/n',T38,'1/n',T48,
     $'CO (ug/L)',T63,'M.W.',/)
      DO 20 I=1,NN*3
       IF (AA(I) .EQ. 1) SR(I)='*'
       IF (AA(I) .NE. 1) SR(I)=' '
20    CONTINUE
      WRITE(7,50) HC(1),P(1),SR(1),P(2),SR(2),P(3),SR(3),MWHC(1)
      IF (NN .GE. 2) WRITE(7,50) HC(2),P(4),SR(4),P(5),SR(5),
     $P(6),SR(6),MWHC(2)
      IF (NN .GE. 3) WRITE(7,50) HC(3),P(7),SR(7),P(8),SR(8),
     $P(9),SR(9),MWHC(3)
      IF (NN .GE. 4) WRITE(7,50) HC(4),P(10),SR(10),P(11),SR(11),
     $P(12),SR(12),MWHC(4)
      IF (NN .GE. 5) WRITE(7,50) HC(5),P(13),SR(13),P(14),SR(14),
     $P(15),SR(15),MWHC(5)
      IF (NN .EQ. 6) WRITE(7,50) HC(6),P(16),SR(16),P(17),SR(17),
     $P(18),SR(18),MWHC(6)
50    FORMAT(1X,A10,T16,F9.4,1X,A1,T33,F9.4,1X,A1,T46,F9.3,1X,
     $A1,T60,F8.3)
C
C              ***CONVERT INITIAL PARAMETERS***
C
      P(2)=1.0D0/P(2)
      P(3)=P(3)/MWHC(1)
      IF (NN .GE. 2) THEN
       P(5)=1.0D0/P(5)
       P(6)=P(6)/MWHC(2)
      ENDIF
      IF (NN .GE. 3) THEN
       P(8)=1.0D0/P(8)
       P(9)=P(9)/MWHC(3)
      ENDIF
      IF (NN .GE. 4) THEN
       P(11)=1.0D0/P(11)
       P(12)=P(12)/MWHC(4)
      ENDIF
      IF (NN .GE. 5) THEN
```

```
       P(14)=1.0D0/P(14)
       P(15)=P(15)/MWHC(5)
      ENDIF
      IF (NN .EQ. 6) THEN
       P(17)=1.0D0/P(17)
       P(18)=P(18)/MWHC(6)
      ENDIF
C
C                  ***COUNT PARAMETERS TO BE VARIED***
C
      NA=0
      DO 60 I=1,NN*3
       IF (AA(I) .EQ. 1) NA=NA+1
       IF (AA(I) .EQ. 1) X(NA)=P(I)
60    CONTINUE
C
C             ***ASSIGN PARAMETERS FOR ZXSSQ***
C
      M=D
      IXJAC=50
      MAXFN=300
C
C  ***CALL ZXSSQ TO FIT THE SINGLE SOLUTE DATA TO MULTICOMPONENT DATA***
C
      PRINT*, 'CALLING ZXSSQ'
      CALL ZXSSQ(IAST,M,NA,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,SSQ,F,XJAC,
     $IXJAC,XJTJ,WORK,INFER,IER)
      PRINT*, 'LEAVING ZXSSQ'
C
C
C            ***WRITE ERROR***
C
      IF (IER .EQ. 133) THEN
       WRITE(7,125)
125    FORMAT(1X,'THE MAXIMUM NUMBER OF ITERATIONS HAS BEEN EXCEEDED')
      ENDIF
C
C           ***CALCULATE THE PERCENT DIFFERENCE***
C
      DO 150 J=1,D
       PD(J)=(CE(J)-CI(1,J))/CE(J)*100.0D0
150   CONTINUE
C
C                ***PUT UNITS BACK TO ug ***
C
      DO 200 J=1,D
       CE(J)=CE(J)*MW
       DO 190 I=1,NC
        IF (I .EQ. 1) THEN
         CI(I,J)=CI(I,J)*MW
         QI(I,J)=QI(I,J)*MW
        ELSE
         CI(I,J)=CI(I,J)*MWHC(I-1)
         QI(I,J)=QI(I,J)*MWHC(I-1)
        ENDIF
```

```
190    CONTINUE
       DM(J)=DM(J)*1000.0D0
200   CONTINUE

C
C                ***PRINT OUT***
C
      PRINT*, 'PRINTING OUTPUT'
      WRITE(7,300) CHAR
300   FORMAT(//,1X,'HYPOTHETICAL COMPONENTS USING   ',A10,'AS THE TRACER
     $')
       IF (RES .EQ. 0) WRITE(7,310)
       IF (RES .EQ. 1) WRITE(7,311)
310   FORMAT(1X,'(RESIDUALS= C(EXP)-C(PRED))')
311   FORMAT(1X,'(RESIDUALS= (C(EXP)-C(PRED))/C(EXP))')
      WRITE(7,400)
400   FORMAT(//,1X,'COMPONENT',T18,'K (um/g)(L/um)**1/n',T40,'1/N',
     $T52,'CO  (um/L)',/)
      WRITE(7,420) CHAR,K,1/XN,CO
      WRITE(7,420) HC(1),B(1),1.0D0/B(2),B(3)
       IF (NN .GE. 2) WRITE(7,420) HC(2),B(4),1.0D0/B(5),B(6)
       IF (NN .GE. 3) WRITE(7,420) HC(3),B(7),1.0D0/B(8),B(9)
       IF (NN .GE. 4) WRITE(7,420) HC(4),B(10),1.0D0/B(11),B(12)
       IF (NN .GE. 5) WRITE(7,420) HC(5),B(13),1.0D0/B(14),B(15)
       IF (NN .EQ. 6) WRITE(7,420) HC(6),B(16),1.0D0/B(17),B(18)
420   FORMAT(2X,A10,T19,F9.4,T36,F9.4,T50,F9.3)
      WRITE(7,425)
425   FORMAT(//,1X,'TRACER RESULTS')
      WRITE(7,430)
430   FORMAT(//,1X,'DOSAGE (mg)',T17,'C (EXP)',T29,'C (IAST)',T41,
     $'Q (IAST)',T53,'% DIFFERENCE',/,1X,T18,'(ug/L)',T30,'(ug/L)'
     $,T42,'(ug/g)',T57,'IN C',/)
      DO 450 J=1,D
       WRITE(7,440) DM(J),CE(J),CI(1,J),QI(1,J),PD(J)
440    FORMAT(1X,F9.4,T15,F9.3,T27,F9.3,T39,F10.3,T54,F8.2)
450   CONTINUE
      WRITE(7,451) HC(1),HC(2),HC(3)
451   FORMAT(///,1X,T19,A10,T38,A10,T58,A10,/,2X,'DOSAGE')
      WRITE(7,452)
452   FORMAT(3X,'(mg)',T12,'C (ug/L)',T22,'Q (ug/g)',T33,'C (ug/L)'
     $,T43,'Q (ug/g)',T54,'C (ug/L)',T64,'Q (ug/g)',/)
      DO 455 J=1,D
       WRITE(7,453) DM(J),CI(2,J),QI(2,J),CI(3,J),QI(3,J),CI(4,J)
     $,QI(4,J)
453   FORMAT(1X,F8.3,T10,F9.5,T20,F10.3,T31,F9.5,T41,F10.3,T52,F9.5,
     $T62,F10.3)
455   CONTINUE
       IF (NC .GT. 4) THEN
        WRITE(7,451) HC(4),HC(5),HC(6)
        WRITE(7,452)
        DO 458 J=1,D
         WRITE(7,453) DM(J),CI(4,J),QI(4,J),CI(5,J),QI(5,J),CI(6,J)
     $,QI(7,J)
458     CONTINUE
       ENDIF
      WRITE(7,459) EPS,NSIG
459   FORMAT(//,1X,'EPS= ',F10.6,5X,'NSIG= ',I2)
      WRITE(7,460) WORK(5)
460   FORMAT(1X,'THE NUMBER OF ITERATIONS =',F6.1)
      WRITE(7,470) WORK(3)
470   FORMAT(1X,'THE ESTIMATED NUMBER OF SIGNIFICANT FIGURES IN THE',/,
     $1X,'PARAMETERS =',F6.1)
      WRITE(7,480) SSQ
480   FORMAT(1X,'THE RESIDUAL SUMS OF SQUARES =',F20.10)
C
      IF (INFER .EQ. 1) WRITE(7,510)
      IF (INFER .EQ. 2) WRITE(7,520)
      IF (INFER .EQ. 3) THEN
       WRITE(7,510)
       WRITE(7,520)
      ENDIF
      IF (INFER .EQ. 4) WRITE(7,540)
      IF (INFER .EQ. 5) THEN
       WRITE(7,510)
       WRITE(7,540)
      ENDIF
      IF (INFER .EQ. 6) THEN
       WRITE(7,520)
       WRITE(7,540)
      ENDIF
      IF (INFER .EQ. 7) THEN
       WRITE(7,510)
       WRITE(7,520)
       WRITE(7,540)
      ENDIF
510   FORMAT(1X,'NO. OF SIGNIFICANT FIGURES CRITERION WAS SATISFIED')
520   FORMAT(1X,'CHANGE IN SUM OF SQUARES CRITERION WAS SATISFIED')
540   FORMAT(1X,'GRADIENT CRITERION WAS SATISFIED')
      WRITE(7,560)
560   FORMAT(/,1X,'* = PARAMETER IS VARIED IN PROGRAM')
1000  STOP
      END
```

```
C
C
C     ******************SUBROUTINE IAST**********************
C
C
C       GIVEN THE FRUENDLICH PARAMETERS FOR THE HYPOTHETICAL
C     COMPONENTS WHICH ARE GENERATED IN ZXSSQ, THIS SUBROUTINE
C     WILL CALCULATE THE LIQUID CONCENTRATION RESIDUALS.  THIS
C     PROGRAM IS BASICALLY THE IAST PROGRAM.
C
C                 ***VARIABLE DEFINITIONS***
C
C      AA    = 0(NO), 1(YES) -IS PREVIOUS PARAMETER TO BE VARIED?
C      B     = FREUNDLICH PARAMETERS TO BE SENT BACK TO PROGRAM
C      CI    = CALCULATED LIQUID-PHASE CONC. (ug/L)- USING IAST
C      CE    = LIQUID-PHASE CONCENTRATIONS (ug/L) - FROM HC PROGRAM
C      CO    = INITIAL CONCENTRATIONS (um/L) -FROM HC PROGRAM
C      D     = NUMBER OF BOTTLE POINTS -FROM HC PROGRAM
C      DM    = DOSAGES OF CARBON (ug)-FROM HC PROGRAM
C      F     = OUTPUT CONTAINING THE RESIDUALS
C      FCN   = SUBROUTINE THAT SETS UP THE NON-LINEAR EQUATIONS
C      FNORM = OUTPUT: EQUAL TO F(1)**2+...F(NC)**2 AT POINT X
C      I     = COUNTER
C      IER   = ERROR PARAMETER
C      ITMAX = THE MAXIMUM NUMBER OF ITERATIONS
C      J     = COUNTER FOR EACH DOSAGE
C      KO    = COUNTER
C      K     = FRUENDLICH K (um/g)(L/um)**1/n -FROM HC PROGRAM
C      L     = COUNTER FOR ADJUSTING ZZ WHEN ERROR IS PRESENT
C      LP    = COUNTER FOR ITERATIONS
C      M     = NUMBER OF DOSAGES
C      MW    = MOLECULAR WEIGHT OF KNOWN COMPONENT -FROM HC PROGRAM
C      N     = NUMBER OF UNKNOWN PARAMETERS
C      NC    = NUMBER OF COMPONENTS
C      NSIGG = NUMBER OF DIGITS OF ACCURACY DESIRED IN COMPUTED ROOT
C      P     = INITIAL PARAMETER GUESS
C      PAR   = PARAMETER SET
C      PAR(1 TO NC)= FRUENDLICH K VALUES
C      PAR(10 TO 10+NC)=FREUNDLICH N VALUES
C      PAR(20 TO 20+NC)= INITIAL CONCENTRATIONS
C      PAR(30)= CARBON DOSAGE
C      PAR(40)= VOLUME OF ISOTHERM BOTTLE
C      QI    = SOLID PHASE CONCENTRATION (ug/g)
C      QT    = TOTAL SURFACE LOADINGS (ug/g)
C      QNQ   = SUM OF Q*XN
C      RES   = COUNTER TO DETERMINE WHICH RESIDUAL IS TO BE USED
C      V     = VOLUMES OF BOTTLES (L) -FROM HC PROGRAM
C      WK    = WORK VECTOR:  LENGTH=N*(3*N+15+)/2
C      X     = FRUENDLICH PARAMETER VALUES
C      XX    = SOLID-PHASE CONCENTRATION (ug/L) -ONE DIMENSION
C      XN    = FRUENDLICH 1/n -FROM HC PROGRAM
C      ZSPOW = SUBROUTINE THE SOLVES THE EQUATIONS
C      ZZ    = VARIABLE USED TO CALCULATE INITIAL Q
C
C
```

```
C                   ***PROGRAM***
C
      SUBROUTINE IAST(X,M,NA,F)
C
C                  ***DIMENSIONING***
C
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION DM(50),V(50),Q(10,50),PAR(50),XX(10),CE(50),WK(621)
     $,F(50),X(18),P(18),B(18),CI(7,50),QI(7,50)
      INTEGER D,RES,AA(18)
      DOUBLE PRECISION K,MW
      EXTERNAL FCN
      COMMON /ZSQ/DM,CO,V,K,XN,D,CE,NN,RES,MW,P,AA,B,CI,QI,NC
C
C              ***ENTER THE PARAMETERS FOR ZSPOW***
C
      KO=0
      PAR(1)=K
      PAR(11)=XN
      PAR(21)=CO
C
      IF (AA(1) .EQ. 1) THEN
       PAR(2)=X(1)
      ELSE
       PAR(2)=P(1)
       KO=KO+1
      ENDIF
      IF (AA(2) .EQ. 1) THEN
       PAR(12)=X(2-KO)
      ELSE
       PAR(12)=P(2)
       KO=KO+1
      ENDIF
      IF (AA(3) .EQ. 1) THEN
       PAR(22)=X(3-KO)
      ELSE
       PAR(22)=P(3)
       KO=KO+1
      ENDIF
C
      IF (NN .GE. 2) THEN
       IF (AA(4) .EQ. 1) THEN
        PAR(3)=X(4-KO)
       ELSE
        PAR(3)=P(4)
        KO=KO+1
       ENDIF
       IF (AA(5) .EQ. 1) THEN
        PAR(13)=X(5-KO)
       ELSE
        PAR(13)=P(5)
        KO=KO+1
       ENDIF
       IF (AA(6) .EQ. 1) THEN
        PAR(23)=X(6-KO)
       ELSE
        PAR(23)=P(6)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .GE. 3) THEN
       IF (AA(7) .EQ. 1) THEN
        PAR(4)=X(7-KO)
       ELSE
        PAR(4)=P(7)
        KO=KO+1
       ENDIF
       IF (AA(8) .EQ. 1) THEN
        PAR(14)=X(8-KO)
       ELSE
        PAR(14)=P(8)
        KO=KO+1
       ENDIF
       IF (AA(9) .EQ. 1) THEN
        PAR(24)=X(9-KO)
       ELSE
        PAR(24)=P(9)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .GE. 4) THEN
       IF (AA(10) .EQ. 1) THEN
        PAR(5)=X(10-KO)
       ELSE
        PAR(5)=P(10)
        KO=KO+1
       ENDIF
       IF (AA(11) .EQ. 1) THEN
        PAR(15)=X(11-KO)
       ELSE
        PAR(15)=P(11)
        KO=KO+1
       ENDIF
       IF (AA(12) .EQ. 1) THEN
        PAR(25)=X(12-KO)
       ELSE
        PAR(25)=P(12)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .GE. 5) THEN
       IF (AA(13) .EQ. 1) THEN
        PAR(6)=X(13-KO)
       ELSE
        PAR(6)=P(13)
        KO=KO+1
       ENDIF
       IF (AA(14) .EQ. 1) THEN
        PAR(16)=X(14-KO)
       ELSE
        PAR(16)=P(14)
        KO=KO+1
       ENDIF
       IF (AA(15) .EQ. 1) THEN
        PAR(26)=X(15-KO)
       ELSE
        PAR(26)=P(15)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .EQ. 6) THEN
       IF (AA(16) .EQ. 1) THEN
        PAR(7)=X(16-KO)
       ELSE
        PAR(7)=P(16)
        KO=KO+1
       ENDIF
       IF (AA(17) .EQ. 1) THEN
        PAR(17)=X(17-KO)
       ELSE
        PAR(17)=P(17)
        KO=KO+1
       ENDIF
       IF (AA(18) .EQ. 1) THEN
        PAR(27)=X(18-KO)
       ELSE
        PAR(27)=P(18)
        KO=KO+1
       ENDIF
      ENDIF
C
C               ***SOLVE EACH DOSAGE INDIVIDUALLY***
C
      NC=1+NN
      DO 1200 J=1,D
       L=0
       ZZ=0.50D0
       PAR(30)=DM(J)
       PAR(40)=V(J)
C
C              ***CALCULATE INITIAL GUESSES ON Q'S***
C
1125   IF (J .EQ. 1) THEN
        DO 1130 I=1,NC
         Q(I,1)=ZZ*PAR(20+I)*V(1)/DM(1)
1130    CONTINUE
       ELSE
        DO 1140 I=1,NC
         Q(I,J)=ZZ*Q(I,J-1)
1140    CONTINUE
       ENDIF
```

```
C
C               ***PUT Q INTO ONE DIMENSIONAL FORM***
C
      DO 1145 I=1,NC
       XX(I)=Q(I,J)
1145  CONTINUE
C
C               ***ENTER OTHER PARAMETERS FOR ZSPOW***
C
      NSIGG=4
1152  N=NC
      ITMAX=100
C
C              ***CALL ZSPOW TO SOLVE THE EQUATIONS***
C
      CALL ZSPOW(FCN,NSIGG,N,ITMAX,PAR,XX,FNORM,WK,IER)
C
C                    ***FIX ANY ERRORS***
C
      IF (IER .EQ. 129 .OR. IER .EQ.131) THEN
       IF (L .EQ. 0) THEN
        ZZ=0.90D0
        L=L+1
        GOTO 1125
       ENDIF
       IF (L .EQ. 1) THEN
        ZZ=0.10D0
        L=L+1
        GOTO 1125
       ENDIF
       IF (L .EQ. 2) THEN
        WRITE(7,1155) DM(J)*1000.0D0
1155    FORMAT(1X,'THERE IS AN ERROR WITH INITIAL CONCENTRATION THE',/,
     $1X,'PROGRAMS INTERNAL FIXING ROUTINE DID NOT HELP. DOSAGE=',F10.4)
       ENDIF
      ENDIF
C
      IF (IER .EQ. 130) THEN
       NSIGG=NSIGG-1
       IF (NSIGG .LT. 0) THEN
        WRITE(7,1160) DM(J)*1000.0D0
1160    FORMAT(1X,'THE NUMBER OF SIGNIFICANT FIGURES HAS DROPPED BELOW
     $ZERO.  THERE ARE NO RESULTS FOR DOSAGE=',F10.4)
        GOTO 1200
       ENDIF
       GOTO 1152
      ENDIF
C
C     ***CALCULATE THE LIQUID CONCENTRATIONS OF COMPONENTS***
C
      DO 1170 I=1,NC
       QI(I,J)=XX(I)
       CI(I,J)=PAR(20+I)-DM(J)/V(J)*QI(I,J)
1170  CONTINUE
C
```

```
C                     ***SET UP RESIDUALS***
C
       IF (RES .EQ. 0) F(J)=CE(J)-CI(1,J)
       IF (RES .EQ. 1) F(J)=(CE(J)-CI(1,J))/CE(J)
C
1200  CONTINUE
C
C               ***SET B TO FINAL PARAMETER VALUES***
C
      B(1)=PAR(2)
      B(2)=PAR(12)
      B(3)=PAR(22)
      IF (NN .GE. 2) THEN
       B(4)=PAR(3)
       B(5)=PAR(13)
       B(6)=PAR(23)
      ENDIF
      IF (NN .GE. 3) THEN
       B(7)=PAR(4)
       B(8)=PAR(14)
       B(9)=PAR(24)
      ENDIF
      IF (NN .GE. 4) THEN
       B(10)=PAR(5)
       B(11)=PAR(15)
       B(12)=PAR(25)
      ENDIF
      IF (NN .GE. 5) THEN
       B(13)=PAR(6)
       B(14)=PAR(16)
       B(15)=PAR(26)
      ENDIF
      IF (NN .EQ. 6) THEN
       B(16)=PAR(7)
       B(17)=PAR(17)
       B(18)=PAR(27)
      ENDIF
C
C                   ***PRINT TO SCREEN***
C

      PRINT*, '           C(1)                           C(D/2)
     $        C(D)'
      PRINT*, CI(1,1)*MW,CI(1,D/2)*MW,CI(1,D)*MW
      PRINT*, '    K (um/g)(L/um)**1/n                     1/n
     $     Co (um/L)'
      DO 1280 I=1,NC-1
       PRINT*, PAR(1+I),1.0D0/PAR(11+I),PAR(21+I)
1280  CONTINUE
      PRINT*, ' '
      RETURN
      END
C
C
C                 *******SUBROUTINE FCN*******
```

```
C
C       THIS SUBROUTINE WILL SET UP THE EQUATIONS THAT WILL BE USED IN
C     THE ZSPOW SUBROUTINE.
C
      SUBROUTINE FCN(XX,F,N,PAR)
C
      DOUBLE PRECISION XX(N),F(N),PAR(50),QNQ,QT
      INTEGER I,N
      QT=0.0D0
      QNQ=0.0D0
      DO 1510 I=1,N
       QT=QT+XX(I)
       QNQ=QNQ+PAR(10+I)*XX(I)
1510  CONTINUE
      DO 1520 I=1,N
       F(I)=PAR(20+I)-PAR(30)/PAR(40)*XX(I)-XX(I)/QT*(QNQ/PAR(10+I)/
     $PAR(I))**PAR(10+I)
1520  CONTINUE
      RETURN
      END
```

Sample Input for the Hypothetical Component Program

```
'DCE',15,46.9,0.5562,1170.0,96.94
2.11,0.160,1110.0
6.11,0.160,1110.0
8.17,0.160,996.0
9.98,0.160,719.0
11.83,0.160,702.8
15.61,0.160,592.3
17.45,0.160,514.8
19.99,0.160,440.1
24.57,0.160,353.8
25.83,0.160,343.2
28.00,0.160,293.7
32.29,0.160,239.4
136.02,0.160,200.7
40.20,0.160,165.8
47.22,0.160,143.5
3
'HC 1',15.1,1,0.8355,1,86.5,1,1.0
'HC 2 (tce)',191.7,0,0.4328,0,120.0,0,131.29
'HC 3 (pce)',435.2,0,0.3847,0,80.0,0,165.83
1
3,0.001,0.0,0
```

Sample Output for the Hypothetical Component Program

```
          INITIAL H.C. GUESSES

COMPONENT     K (um/g)(L/um)**1/n      1/n          CO (ug/L)        M.W.

HC 1              10.0000 *           0.8000 *       80.000 *        1.000
HC 2 (tce)       191.7000             0.4328        120.000        131.290
HC 3 (pce)       435.2000             0.3847         80.000        165.830

HYPOTHETICAL COMPONENTS USING   DCE        AS THE TRACER
(RESIDUALS= (C(EXP)-C(PRED))/C(EXP))

COMPONENT        K (um/g)(L/um)**1/n    1/N           CO  (um/L)

 DCE                  46.9000           0.5562         12.069
 HC 1                 15.1180           0.8355         86.504
 HC 2 (tce)          191.7000           0.4328          0.914
 HC 3 (pce)          435.2000           0.3847          0.482

TRACER RESULTS

DOSAGE (mg)     C (EXP)      C (IAST)      Q (IAST)     % DIFFERENCE
                 (ug/L)       (ug/L)        (ug/g)          IN C

   2.1100      1110.000     1048.915      9181.774          5.50
   6.1100      1110.000      833.619      8808.670         24.90
   8.1700       996.000      742.950      8363.277         25.41
   9.9800       719.000      673.345      7962.408          6.35
  11.8300       702.800      610.713      7564.319         13.10
  15.6100       592.300      504.987      6816.275         14.74
  17.4500       514.800      462.443      6487.630         10.17
  19.9900       440.100      411.471      6071.269          6.51
  24.5700       353.800      337.719      5419.818          4.55
  25.8300       343.200      320.745      5260.582          6.54
  28.0000       293.700      294.261      5004.220         -0.19
  32.2900       239.400      250.450      4556.459         -4.62
 136.0200       200.700       30.313      1340.611         84.90
  40.2000       165.800      191.348      3895.131        -15.41
  47.2200       143.500      154.681      3440.302         -7.79


                 HC 1                   HC 2 (tce)             HC 3 (pce)
 DOSAGE
  (mg)     C (ug/L)   Q (ug/g)     C (ug/L)   Q (ug/g)     C (ug/L)   Q (ug/g)

  2.110  80.33475     467.798    46.71484    5557.168    5.14502    5676.207
  6.110  69.65497     441.214    17.15971    2693.035    1.34608    2059.677
  8.170 65.00151     421.098  12.19639   2111.209   0.90004    1549.081
  9.980 61.31999     403.749   9.47409   1771.959   0.67310    1271.774
 11.830 57.90218     386.836   7.55540   1520.806   0.52063    1074.953
 15.610 51.83577     355.342   5.10022   1177.704   0.33491     816.554
 17.450 49.26028     341.488   4.31754   1060.699   0.27811     730.974
 19.990 46.04553     323.828   3.49953    932.470   0.22015     638.558
 24.570 41.08193     295.788   2.50722    765.114   0.15204     519.970
 25.830 39.87561     288.831   2.30642    729.035   0.13859     494.689
 28.000 37.93618     277.529   2.01164    674.219   0.11911     456.462
 32.290 34.54983     257.437   1.56943    586.835   0.09044     395.959
136.020  9.63422      90.422   0.08858    141.052   0.00368      94.099
 40.200 29.53023     226.761   1.05529    473.412   0.05823     318.176
 47.220 26.05416     204.827   0.77961    403.966   0.04161     270.931


EPS=   0.010000     NSIG=  2
THE NUMBER OF ITERATIONS =   2.0
THE ESTIMATED NUMBER OF SIGNIFICANT FIGURES IN THE
PARAMETERS =   1.4
THE RESIDUAL SUMS OF SQUARES =         0.9461127603
CHANGE IN SUM OF SQUARES CRITERION WAS SATISFIED

* = PARAMETER IS VARIED IN PROGRAM
```

APPENDIX X. THE EQUILIBRIUM COLUMN MODEL DEVELOPMENT

By Thomas F. Speth, David W. Hand, John C. Crittenden, Paul J. Luft

The liquid phase concentration for any component i in zone k+1 is determined from a mass balance on a wave front as shown in Figure V-2. The liquid phase concentrations in zone 1 are the influent concentrations to the bed. Therefore, for any component i in zone k, the following mass balance on wave front k-1 on component i can be derived.

$$\begin{matrix}\text{rate of change}\\ \text{solid phase}\\ \text{concentration}\end{matrix} + \begin{matrix}\text{rate of change}\\ \text{liquid phase}\\ \text{concentration}\end{matrix} = \begin{matrix}\text{rate of}\\ \text{accumulation}\\ \text{in front k-1}\end{matrix} \tag{VII-24}$$

From Figure V-2, the rate of change of solid phase concentration can be calculated if the velocity of front k-1, Vw_{k-1} moving through the bed is known.

$$\begin{matrix}\text{rate of change}\\ \text{solid phase}\\ \text{concentration}\end{matrix} = (q_{i,k} - q_{i,k-1})\rho_B Vw_{k-1} A_b \tag{VII-25}$$

Where, A_b is the cross sectional area of the column, ρ_B is the bulk density of the column, and q represents the solid phase concentration.

The rate of change in the liquid phase concentration can be calculated knowing the velocity of the front (Vw_{k-1}) and the velocity of the fluid (Vf).

$$\begin{matrix}\text{rate of change}\\ \text{liquid phase}\\ \text{concentration}\end{matrix} = (C_{i,k-1} - C_{i,k})(V_f - Vw_{k-1})\varepsilon A_b \tag{VII-26}$$

Where, ε is the bed void fraction, and C is the liquid phase concentration. Since the wave front has no volume, the accumulation in front k-1 is zero. Solving the mass balance for $C_{i,k}$ yields:

$$C_{i,k} = \frac{(q_{i,k} - q_{i,k-1})\rho_B Vw_{k-1}}{(V_f - Vw_{k-1})\ \varepsilon} + C_{i,k-1} \tag{VII-27}$$

The wave velocity, Vv_k can be determined from a mass balance over the entire bed length at time t_k, when zone k just breaks through for component i.

$$\begin{array}{c}\text{Total Mass}\\ \text{In}\end{array} - \begin{array}{c}\text{Total Mass}\\ \text{Out}\end{array} = \begin{array}{c}\text{accumulation}\\ \text{in solid}\\ \text{phase}\end{array} + \begin{array}{c}\text{accumulation}\\ \text{in liquid}\\ \text{phase}\end{array} \tag{VII-28}$$

The total mass in is calculated from the flow rate (Q) and initial concentration for each component (Co_i).

$$\begin{array}{c}\text{Total Mass}\\ \text{In}\end{array} = Qt_k \, Co_i \tag{VII-29}$$

Up to time t_k, the total mass out of component i is zero. The accumulation in the solid phase will be the sum of the solid-phase concentrations in each zone.

$$\begin{array}{c}\text{Accumulation}\\ \text{in solid}\\ \text{phase}\end{array} = \sum_{j=1}^{k} q_{i,j} \, \rho_B Vm_j \qquad i = 1, N \tag{VII-30}$$

Where Vm_j is the volume of zone j. The accumulation in the liquid-phase will be the sum of the liquid-phase accumulations in each zone.

$$\begin{array}{c}\text{Accumulation}\\ \text{in liquid}\\ \text{phase}\end{array} = \sum_{j=1}^{k} C_{i,j} \, \varepsilon \, Vm_j \qquad i = 1, N \tag{VII-31}$$

Substituting Equations VII-29, VII-30, and VII-31 into Equation VII-28.

$$Qt_k \, Co_i = \sum_{j=1}^{k} [(q_{i,j}\rho_B + C_{i,j}\varepsilon)Vm_j] \tag{VII-32}$$

To relate the volume of a zone to the velocities of each wave front which separates each zone.

$$Vm_j = (Vw_j - Vw_{j-1}) \, A_b \, t_k \tag{VII-33}$$

The flowrate can be converted to the interstitial velocity of the fluid (V_f).

$$Q = A_b \varepsilon V_f \tag{VII-34}$$

Substituting Equations VII-33 and VII-34 into equation VII-32 and solving for Vw_k yields:

$$Vw_k = \frac{V_f \varepsilon Co_i - \sum_{j=1}^{k-1} [(q_{i,j} \rho_B + C_{i,j} \varepsilon)(Vw_j - Vw_{j-1})] + (q_{i,k} \rho_\beta + C_{i,k} \varepsilon) Vw_{k-1}}{(q_{i,k} \rho_B + C_{i,k} \varepsilon)} \tag{VII-35}$$

Equations VII-27 and VII-35 combined with ideal adsorbed solution theory can describe the bed performance given the single solute Freundlich isotherm parameters, the initial concentrations for each component, the liquid loading to the bed, and the bed bulk bed density and porosity.

METHOD OF SOLUTION

All the overshoot concentrations and wave front velocities can be determined using a stepwise zone by zone procedure.

Zone 1

In zone 1 the liquid-phase concentrations are at their initial values, therefore only the solid-phase concentrations are unknown and can be calculated using IAST. There will be N equations and N unknowns. The following IAST equation can be used to obtain the surface loadings for each component in zone 1.

$$C_{i,1} = \frac{q_{i,1}}{\sum_{j=1}^{N} q_{j,1}} \left[\frac{\sum_{j=1}^{N} n_j \, q_{j,1}}{n_i \, k_i} \right]^{n_i} \qquad (i = 1,N) \qquad \text{(VII-36)}$$

Since all of the liquid-phase concentrations in zone 1 are at their known influent values, Equation VII-36 may be written as:

$$F_i(q_1,q_2,\ldots,q_i,\ldots,q_n) = -Co_i + \frac{q_{i,1}}{\sum_{j=1}^{N} q_{j,1}} \left[\frac{\sum_{j=1}^{N} n_j \, q_{j,1}}{n_i \, k_i} \right]^{n_i} \qquad (i = 1,N) \qquad \text{(VII-37)}$$

According to Equation VII-37, the equilibrium state is given by the zero roots. Furthermore, all that is needed to define the equilibrium state are the Freundlich K and 1/n, and the initial liquid-phase concentration of each solute.

The velocity of the wavefront of zone 1 is obtained from Equation VII-35 which reduces to the following equation:

$$Vw_1 = \frac{V_f \, Co_1 \, \varepsilon}{(q_{1,1} \, \rho_B + Co_1 \, \varepsilon)} \qquad \text{(VII-38)}$$

FOLLOWING ZONES

For zone k (where k is greater than one), there is K = k to N equations because components 1 through k-1, the strongest components, are only present in the earlier zones. In this zone both the $C_{i,k}$'s and $q_{i,k}$'s are unknown, therefore, we must combine Equation VII-36 for zone i with Equation VII-27 to obtain a series of k through N equations expressed in terms of $q_{i,k}$ only. The following equation is obtained.

$$\frac{q_{i,k}}{\sum_{j=k}^{N} q_{j,k}} \left[\frac{\sum_{j=k}^{N} n_j q_{j,k}}{n_i\ k_i} \right]^{ni} = \frac{(q_{i,k} - q_{i,k-1}) \rho_B Vw_{k-1}}{(V_f - Vw_{k-1})\ \varepsilon} + C_{i,k-1} \qquad \text{(VII-39)}$$

Equation VII-39 can than be written in terms of the equations zero roots.

$$\overset{->}{F}(q_1, q_2, \ldots, q_i, \ldots q_n) = - \frac{q_{i,k}}{\sum_{j=k}^{N} q_{j,k}} \left[\frac{\sum_{k=k}^{N} n_j\ q_{j,k}}{n_i\ k_i} \right]^{n_i}$$

$$+ \frac{(q_{i,k} - q_{i,k-1}) \rho_B\ Vw_{k-1}}{(V_f + Vw_{k-1})\ \varepsilon} + C_{i,k-1} \qquad \text{(VII-40)}$$

The liquid-phase concentrations ($C_{i,k}$) can then be obtained from Equation VII-27, and the velocity with which wave i moves through the bed can be obtained from Equation VII-35.

Once all the liquid and solid-phase concentrations have been determined, the maximum number of bed volumes fed to breakthrough for each compound can be determined using the following equation:

$$BVF_i = \frac{\sum_{k=1}^{N} [(q_{i,k}\rho_B + C_{i,k}\varepsilon)(Vw_k - Vw_{k-1})]}{Co_i \; Vw_i} \quad \text{(VII-41)}$$

APPENDIX XI. COMPUTER CODE FOR THE EQUILIBRIUM COLUMN MODEL

```
C
C
C                  ********EQUILIBRIUM THEORY PROGRAM********
C
C
C     THIS PROGRAM CALCULATES MULTICOMPONENT BREAKTHROUGH FOR FIXED
C     BED ADSORBERS. THE PROGRAM ASSUMES NO MASS TRANSFER RESISTANCE.
C     IDEAL ADSORBED SOLUTION THEORY IS USED TO PREDICT COMPETITION.
C
C     THE OUTPUT FILE WILL CONTAIN A LISTING OF THE INPUT PARAMETERS.
C     THIS IS FOLLOWED BY THE NUMBER OF BED VOLUMES FED TO BREAK-
C     THROUGH, THE VELOCITY OF THE WAVE, AND THE TREATMENT CAPACITY
C     FOR EACH ZONE.  THE INDIVIDUAL COMPONENTS ARE THEN PRINTED IN
C     ORDER OF DECREASING STRENGTH OF ADSORPTION.  FOR EACH
C     INDIVIDUAL COMPONENT, THE FREUNDLICH K AND 1/n, INFLUENT
C     CONCENTRATION, AND THE MOLECULAR WEIGHT ARE PRINTED ALONG WITH
C     THE SINGLE SOLUTE TREATMENT CAPACITY, AND THE DIMENSIONLESS BED
C     LENGTH FOR THE LAST ZONE.  ALSO INCLUDED IS THE LIQUID AND
C     PHASE CONCENTRATIONS, THE DIMENSIONLESS LIQUID PHASE
C     CONCENTRATIONS, A DIMENSIONLESS GROUP USED TO FIND THE STRONGEST
C     ADSORBING COMPOUND IN EACH ZONE, THE AVERAGE SOLID PHASE
C     CONCENTRATION UP TO THAT ZONE, AND THE Cio'S USED IN THE
C     IAST CALCULATIONS.  ACCORDING TO THE IAST DEVELOPMENT, THE
C    Cio'S MUST LIE WITHIN THE CONCENTRATION RANGE OF THE SINGLE
C     SOLUTE ISOTHERM USED TO FIND THE FREUNDLICH CONSTANTS TO
C     ASSUME CONSTANT SPREADING PRESSURES, AN
C     ASSUMPTION OF IAST.
C
C
C     PROGRAM WRITTEN BY:  THOMAS F. SPETH, PAUL LUFT, DAVID HAND,
C                          AND DR. JOHN CRITTENDEN
C
C
C     PROGRAM LANGUAGE:  FORTRAN-77
C
C
C                            VARIBLE DEFINITIONS
C
C     BVF   = BED VOID FRACTION
C     C     = LIQUID PHASE CONCENTRATION (ug/L)
C     CH    = WORKING CHARACTER
C     CHAR  = NAME OF THE COMPONENTS (TEN LETTERS)
C     CO    = INITIAL CONCENTRATIONS (ug/L)
C     DEN   = BULK DENSITY OF ADSORBENT (g/cm**3)
C     DGX   = DIMENSIONLESS GROUP X:  USED TO FIND STRONGEST COMPONENT
C     DGY   = DIMENSIONLESS GROUP Y:  USED TO FIND STRONGEST COMPONENT
C     FCN   = SUBROUTINE THAT SETS UP THE NON-LINEAR EQUATIONS
C     FCS   = C/CO
C     FLRT  = FLOW RATE (GPM/FT**2)
C     FNORM = OUTPUT:  SUM OF THE RESIDUALS
C     I     = COUNTER
```

```
C     IAST  = SUBROUTINE TO ACCOUNT FOR COMPETITIVE EFFECTS
C     IER   = OUTPUT:  ERROR PARAMETER
C     ITMAX = MAXIMUM NUMBER OF ITERATIONS
C     IX    = USED TO KEEP TRACK OF STRONGEST COMPONENT
C     J     = COUNTER
C     K     = COUNTER
C     L     = COUNTER FOR ERROR FIXING
C     M     = COUNTER
C     MW    = MOLECULAR WEIGHT
C     N     = NUMBER OF COMPONENTS TOTAL
C     NN    = NUMBER OF COMPONENTS IN A ZONE
C     NS    = NSIG INPUT
C     NSIG  = NUMBER OF DIGITS OF ACCURACY DESIRED IN THE COMPUTED ROOT
C     OATS  = BED VOLUMES FED
C     PAR   = PARAMETER SET
C     PAR(1 to N)= FREUNDLICH K VALUES
C     PAR(10 to 10+N)= FRUENDLICH N VALUES
C     PAR(20 to 20+N)= INITIAL CONCENTRATIONS
C     PAR(30)= VELOCITY OF THE WAVE: VW (cm/s)
C     PAR(35)= VELOCITY OF FLOW: VF (cm/s)
C     PAR(40 to 40+I)= CALCULATED LIQUID CONCENTRATIONS
C     PAR(60 to 60+I)= Q's OF THE PREVIOUS WAVE
C     PAR(80 to 80+I)= C's OF THE PREVIOUS WAVE
C     Q     = SOLID PHASE CONCENTRATION (ug/g)
C     QAVE  = AVERAGE Q IN ZONE
C     SSTC  = SINGLE SOLUTE TREATMENT CAPACITY (mg C/L WATER)
C     SUM   = USED TO CALCULATE VW AND OATS
C     VF    = VELOCITY OF FLOW (cm/s)
C     VW    = VELOCITY OF WAVE (cm/s)
C     WK    = WORK VECTOR:  LENGTH=N*(3*N+15)/2
C     X     = ONE DIMENSIONAL SOLID-PHASE CONCENTRATION (um/g)
C     XK    = FREUNDLICH K's (um/g)*((L/um)**1/N
C     XN    = FRUENDLICH 1/n 's
C     ZSQ   = COMMON BLOCK
C     ZZ    = VARIABLE USED TO CALCULATE INITIAL Q's
C     ZZZ   = DIMENSIONLESS BED LENGTH
C
C
C                          SAMPLE INPUT
C
C            N,BVF,DEN,FLRT
C            CHAR(I),XK(I),XN(I),CO(I),MW(I)
C            ....    ..    ..    ..    ..
C            CHAR(J),XK(J),XN(J),CO(J),MW(J)
C            NS
C
C                           DIMENSIONS
C
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      CHARACTER*40 CHAR(20),CH
      DOUBLE PRECISION MW(20)
      DIMENSION XN(20),XK(20),CO(20,20),C(20,20),Q(20,20),ZZZ(20),VW(20)
     $,DGY(20,20),OATS(20),QAVE(20,20),SSTC(20),WK(200),X(20)
     $,PAR(100),FCS(20,20),CIO(20,20)
      EXTERNAL FCN
      COMMON /ZSQ/ BVF,DEN,M
C
C                        OPEN FILES
C
      OPEN(4,FILE='ET.DAT')
      OPEN(7,FILE='ET.OUT')
C
C                       READ IN DATA
C
      PRINT*, 'READING DATA'
      READ(4,*) N,BVF,DEN,FLRT
      DO 10 I=1,N
       READ(4,*) CHAR(I),XK(I),XN(I),CO(I,1),MW(I)
       CO(I,1)=CO(I,1)/MW(I)
       XN(I)=1.0D0/XN(I)
10    CONTINUE
C
C                        CHANGE UNITS
C
      VF=FLRT*0.067910D0/BVF
      DEN=DEN*1000.0D0
C
C               SET ZONE ONE CONCENTRATIONS TO ZERO
C
      DO 20 I=1,N
       VW(I)=0.0D0
       PAR(60+I)=0.0D0
       PAR(80+I)=0.0D0
20    CONTINUE
C
C                 SOLVE FOR EACH ZONE SEPARATELY
C
      DO 100 J=1,N
      PRINT*, 'SOLVING FOR ZONE ',J
C
      L=0
      M=J
      NS=9
      NN=N+1-J
      ZZ=1.0D0
      NSIG=NS
      SUM=0.0D0
C
C               CALCULATE INITIAL GUESSES OF Q's
C
21      DO 22 I=1,N
         Q(I,J)=ZZ*XK(I)*CO(I,J)**(1.0D0/XN(I))
22      CONTINUE
C
C               PUT Q INTO ONE-DIMENSIONAL FORM
C
       DO 24 I=1,N
        X(I)=Q(I,J)
24     CONTINUE
C
```

```
C                   SET IAST PARAMETERS
C
      DO 26 I=1,NN
       X(I)=X(M-1+I)
       PAR(I)=XK(M-1+I)
       PAR(10+I)=XN(M-1+I)
       PAR(20+I)=CO(M-1+I,J)
       PAR(60+I)=PAR(60+M-1+I)
       PAR(80+I)=PAR(80+M-1+I)
26    CONTINUE
      PAR(30)=VW(J-1)
      PAR(35)=VF
      ITMAX=100
C
      CALL ZSPOW(FCN,NSIG,NN,ITMAX,PAR,X,FNORM,WK,IER)
C
C                       FIX ANY ERRORS
C
      IF (IER .EQ. 129 .OR. IER .EQ. 131) THEN
       IF (L .EQ. 0) THEN
        ZZ=2.0D0*ZZ
        L=L+1
        GOTO 21
       ENDIF
       IF (L .EQ. 1) THEN
        ZZ=3.0D0*ZZ
        L=L+1
        GOTO 21
       ENDIF
       IF (L .EQ. 2) THEN
        ZZ=ZZ/20.0D0
        L=L+1
        GOTO 21
       ENDIF
       IF (L .EQ. 3) THEN
        WRITE(7,28) J
28      FORMAT(1X,'THERE IS A PROBLEM WITH THE INITIAL CONCENTRATIONS',
     $/,'THAT THE PROGRAMS FIXING ROUTINE DID NOT HELP.  ZONE=',I2)
       ENDIF
      ENDIF
C
      IF (IER .EQ. 130) THEN
       NSIG=NSIG-1
       IF (NSIG .LT. 0) THEN
        WRITE(7,29) J
29      FORMAT(1X,'THE NUMBER OF SIGNIFICANT FIGURES HAS DROPPED BELOW
     $ZERO.  THERE ARE NO RESULTS FOR ZONE',I2)
       ENDIF
       GOTO 21
      ENDIF
C
C           SET X TO TWO-DIMENSIONAL OUTPUT FOR PRINT OUT
C
      IF (M .GT. 1) THEN
       DO 30 I=1,M-1
```

```
           Q(I,J)=0.0D0
30        CONTINUE
         ENDIF
         DO 31 I=1,NN
          Q(I+M-1,J)=X(I)
31       CONTINUE
C
C                CALCULATE THE LIQUID CONCENTRATIONS
C
         IF (M .GT. 1) THEN
          DO 33 I=1,M-1
           C(I,J)=0.0D0
33        CONTINUE
         ENDIF
         DO 34 I=1,NN
          C(I+M-1,J)=PAR(40+I)
34       CONTINUE
C
C             DETERMINE THE STRONGEST COMPONENT IN ZONE J
C
         DGX=0.0D0
         DO 35 I=M,N
          DG=DEN*Q(I,J)/(C(I,J)*BVF)
          IF (DG .GT. DGX) THEN
           DGX=DG
           IX=I
          ENDIF
35       CONTINUE
C
C                     SET STRONGEST COMPONENT TO ZONE J
C
         CH=CHAR(IX)
         CHAR(IX)=CHAR(J)
         CHAR(J)=CH
C
         WM=MW(IX)
         MW(IX)=MW(J)
         MW(J)=WM
C
         XXK=XK(IX)
         XK(IX)=XK(J)
         XK(J)=XXK
C
         XXN=XN(IX)
         XN(IX)=XN(J)
         XN(J)=XXN
C
        DO 37 K=1,J
         XCO=CO(IX,K)
         CO(IX,K)=CO(J,K)
         CO(J,K)=XCO
C
          XC=C(IX,K)
          C(IX,K)=C(J,K)
          C(J,K)=XC
```

```
C
        XQ=Q(IX,K)
        Q(IX,K)=Q(J,K)
        Q(J,K)=XQ
37     CONTINUE
C
C                 SET C's AND Q's FOR NEXT ZONE
C
       DO 38 I=1,N
        PAR(60+I)=Q(I,J)
        PAR(80+I)=C(I,J)
38     CONTINUE
C
C           CALCULATE VELOCITY OF THE WAVE FOR ZONE J
C
       IF (J .EQ. 1) THEN
        VW(J)=VF*BVF*CO(1,J)/(Q(1,J)*DEN+C(1,J)*BVF)
       ENDIF
       IF (J .GE. 2) THEN
        SUM=(Q(J,1)*DEN+BVF*C(J,1))*VW(1)
       ENDIF
       IF (J .GT. 2) THEN
        DO 40 K=2,J-1
         SUM=SUM+((Q(J,K)*DEN+BVF*C(J,K))*(VW(K)-VW(K-1)))
40      CONTINUE
       ENDIF
       IF (J .GE. 2) THEN
        VW(J)=(BVF*VF*CO(J,J)-SUM+(Q(J,J)*DEN+BVF*C(J,J))*VW(J-1)
     $)/(Q(J,J)*DEN+BVF*C(J,J))
       ENDIF
C
C                     SET Co FOR NEXT ZONE
C
       DO 50 I=J+1,N
        CO(I,J+1)=C(I,J)
50     CONTINUE
       DO 60 I=1,J
        CO(I,J+1)=0.0D0
60     CONTINUE
C
100   CONTINUE
C
C                    CALCULATE BED VOLUMES FED
C
      PRINT*, 'CALCULATING VARIOUS PARAMETERS'
      DO 110 I=1,N
       SUM=(Q(I,1)*DEN+C(I,J)*BVF)*VW(1)
       IF (I .GE. 2) THEN
        DO 105 K=2,I
         SUM=SUM+(Q(I,K)*DEN+C(I,K)*BVF)*(VW(K)-VW(K-1))
105     CONTINUE
       ENDIF
       OATS(I)=SUM/(CO(I,I)*VW(I))
110   CONTINUE
C
```

```
C               CALCULATE Q  TOTAL AVERAGE FOR EACH ZONE
C
      DO 120 I=1,N
       QAVE(I,1)=Q(I,1)
120   CONTINUE
      DO 140 I=1,N
       DO 130 J=2,N
        QAVE(I,J)=(QAVE(I,J-1)*VW(J-1)+Q(I,J)*(VW(J)-VW(J-1)))/VW(J)
130    CONTINUE
140   CONTINUE
C
C                  CALCULATE DIMENSIONLESS BED LENGTH
C
      DO 150 I=1,N
       IF (I .EQ. 1) THEN
        ZZZ(1)=0.0D0
       ELSE
        ZZZ(I)=VW(I-1)/VW(N)
       ENDIF
       ZZZ(I)=VW(I)/VW(N)-ZZZ(I)
150   CONTINUE
C
C            CALCULATE SINGLE SOLUTE TREATMENT CAPACITY
C
      DO 160 I=1,N
       SSTC(I)=1000.0D0*CO(I,1)**(1.0D0-1.0D0/XN(I))/XK(I)
160   CONTINUE
C
C                   CALCULATE DG's FOR PRINT OUT
C
      DO 180 J=1,N
       DO 170 I=1,N
        DGY(I,J)=DEN*Q(I,J)/(C(I,J)*BVF)
        IF (C(I,J) .EQ. 0.0) DGY(I,J)=0.0
170    CONTINUE
180   CONTINUE
C
C                   CALCULATE C/Co FOR PRINT OUT
C
      DO 195 J=1,N
       DO 190 I=1,N
        FCS(I,J)=C(I,J)/CO(I,J)
        IF (CO(I,J) .EQ. 0.0) FCS(I,J)=0.0
190    CONTINUE
195   CONTINUE
C
C                    CALCULATE Cio
C
      DO 250 J=1,N
       CISUM=0.0D0
       DO 230 I=1,N
        CISUM=CISUM+XN(I)*Q(I,J)
230    CONTINUE
       DO 240 I=1,N
        CIO(I,J)=(CISUM/XN(I)/XK(I))**XN(I)
```

```
240     CONTINUE
250    CONTINUE
C
C                        PUT INTO ug/L UNITS
C
       DO 210 J=1,N
        DO 200 I=1,N
         CO(I,J)=CO(I,J)*MW(I)
         CIO(I,J)=CIO(I,J)*MW(I)
         Q(I,J)=Q(I,J)*MW(I)
         QAVE(I,J)=QAVE(I,J)*MW(I)
         C(I,J)=C(I,J)*MW(I)
200     CONTINUE
210    CONTINUE
C
C                       PRINT RESULTS
C
       PRINT*, 'PRINTING OUTPUT'
       WRITE(7,900)
900    FORMAT(//,1X,T10,'EQUILIBRIUM THEORY RESULTS')
       WRITE(7,910) N,BVF,DEN/1000.0D0,FLRT
910    FORMAT(1X,//,T10,'NUMBER OF COMPONENTS :',T54,I2,/,
      $T10,'BED VOID FRACTION :',T55,F5.3,/,
      $T10,'BULK DENSITY OF ADSORBENT (g/cm**3) :',T50,F10.3,/,
      $T10,'FLOWRATE (gpm/ft**2) :',T50,F10.3,//)
       WRITE(7,920)
920    FORMAT(T19,'BED VOLUMES FED',T36,'VELOCITY OF WAVE',T54,
      $'TREATMENT CAPACITY',/,
      $T19,'TO BREAKTHROUGH',T40,'(cm/sec)',T54,'(mg CARBON/L WATER)',/)
       DO 940 I=1,N
        WRITE(7,930) I,OATS(I),VW(I),DEN*1000.0D0/OATS(I)
930     FORMAT(T8,'ZONE(',T13,I2,T15,')',T17,F13.1,T36,E15.8,T52,F15.4)
940    CONTINUE
       DO 1000 I=1,N
        WRITE(7,950) CHAR(I),XK(I),1.0D0/XN(I),CO(I,1),MW(I),SSTC(I),I,
      $ ZZZ(I)
950     FORMAT(//,'COMPONENT= ',A40,//,
      $ T10,'FREUNDLICH K (um/g)*(L/um)**1/n :',T45,F10.2,/,
      $ T10,'FREUNDLICH 1/n :',T45,F10.4,/,
      $ T10,'INITIAL CONCENTRATION (ug/L) :',T45,F10.4,/,
      $ T10,'MOLECULAR WEIGHT :',T45,F10.4,/,
      $ T10,'SINGLE SOLUTE TREATMENT CAPACITY',/,
      $ T12,'(mg CARBON/L WATER) :',T40,F15.4,/,
      $ T10,'DIMENSIONLESS BED LENGTH',/,
      $ T12,'FOR ZONE(',T21,I2,T23,') :',T45,F10.8,//,
      $ T12,'C(ug/L)',T24,'Q(ug/g)',T35,'C/Co',T46,'DG',T56,'QAVE',T63,
      $ 'Cio (ug/L)')
        DO 970 J=1,N
         WRITE(7,960) J,C(I,J),Q(I,J),FCS(I,J),DGY(I,J),QAVE(I,J),
      $  CIO(I,J)
960      FORMAT('ZONE(',T7,I2,T9,')',T11,F9.3,T22,F10.2,T33,
      $F7.4,T43,E8.3,T52,F10.2,T63,E10.3)
970      CONTINUE
1000   CONTINUE
       STOP
      END
C
C
C                      SUBROUTINE FCN
C
C      THIS SUBROUTINE WILL SET UP THE EQUATIONS THAT WILL BE USED IN
C    THE ZSPOW SUBROUTINE.
C
C
      SUBROUTINE FCN(X,F,NN,PAR)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION X(NN),F(NN),PAR(100)
      COMMON /ZSQ/ BVF,DEN,M
      PRINT*, 'M=',M
      QT=0.0D0
      QNQ=0.0D0
      DO 1010 I=1,NN
       QT=QT+X(I)
       QNQ=QNQ+PAR(10+I)*X(I)
1010  CONTINUE
C
C                       CALCULATE F(I)
C
      IF (M .EQ. 1) THEN
       DO 1020 I=1,NN
        F(I)=-PAR(20+I)+X(I)/QT*(QNQ/PAR(10+I)/PAR(I))**PAR(10+I)
1020   CONTINUE
      ENDIF
      IF (M .GT. 1) THEN
       DO 1030 I=1,NN
        F(I)=-X(I)/QT*(QNQ/PAR(10+I)/PAR(I))**PAR(10+I)+((X(I)-PAR(60+I)
     $)*DEN*PAR(30))/((PAR(35)-PAR(30))*BVF)+PAR(80+I)
1030   CONTINUE
      ENDIF
C
C                 CALCULATE LIQUID CONCENTRATION
C
      IF (M .EQ. 1) THEN
       DO 1040 I=1,NN
        PAR(40+I)=X(I)*(QNQ/(PAR(10+I)*PAR(I)))**PAR(10+I)/QT
        PRINT*, 'X(I) ',X(I),'   F(I) ',F(I)
1040   CONTINUE
      ENDIF
      IF (M .GT. 1) THEN
       DO 1050 I=1,NN
        PAR(40+I)=((X(I)-PAR(60+I))*DEN*PAR(30))/((PAR(35)-PAR(30))
     $*BVF)+PAR(80+I)
        PRINT*, 'X(I) ',X(I),' F(I) ',F(I)
1050   CONTINUE
      ENDIF
      RETURN
      END
```

Sample Input - Equilibrium Column Model Program

```
7,0.431,0.457,1.931
'M-XYLENE',1044.0,0.2458,5.2,106.17
'OP-XYLENE',895.0,0.2587,9.3,106.17
'ETHYL BENZENE',714.4,0.2953,4.5,106.17
'TOLUENE',475.0,0.3282,19.3,92.15
'TETRACHLOROETHENE',435.0,0.3847,37.6,165.83
'TRICHLOROETHENE',192.0,0.4328,47.9,131.29
'CIS-DICHLOROETHENE',46.9,0.5562,70.9,96.93
```

Sample Output - Equilibrium Column Model Program

```
        EQUILIBRIUM THEORY RESULTS

        NUMBER OF COMPONENTS :                          7
        BED VOID FRACTION :                             0.431
        BULK DENSITY OF ADSORBENT (g/cm**3) :           0.457
        FLOWRATE (gpm/ft**2) :                          1.931

                 BED VOLUMES FED   VELOCITY OF WAVE  TREATMENT CAPACITY
                 TO BREAKTHROUGH      (cm/sec)      (mg CARBON/L WATER)

      ZONE( 1)     2927945.1      0.44787107E-07          0.1561
      ZONE( 2)     1705417.4      0.76892724E-07          0.2680
      ZONE( 3)     1160827.3      0.11296615E-06          0.3937
      ZONE( 4)      379562.6      0.34548770E-06          1.2040
      ZONE( 5)      270725.2      0.48438112E-06          1.6881
      ZONE( 6)      113547.0      0.11548895E-05          4.0248
      ZONE( 7)       22398.9      0.58544937E-05         20.4028

COMPONENT= M-XYLENE

        FREUNDLICH K (um/g)*(L/um)**1/n :      1044.00
        FREUNDLICH 1/n :                         0.2458
        INITIAL CONCENTRATION (ug/L) :           5.2000
        MOLECULAR WEIGHT :                     106.1700
        SINGLE SOLUTE TREATMENT CAPACITY
          (mg CARBON/L WATER) :                  0.0985
        DIMENSIONLESS BED LENGTH
          FOR ZONE( 1) :                       0.00765004

             C(ug/L)     Q(ug/g)    C/Co       DG        QAVE    Clo (ug/L)
ZONE(   1)    5.200     33315.79   1.0000   .679E+07   33315.79  0.103E+02
ZONE(   2)    0.000         0.00   0.0000   .000E+00   19405.19  0.645E+01
ZONE(   3)    0.000         0.00   0.0000   .000E+00   13208.54  0.134E+01
ZONE(   4)    0.000         0.00   0.0000   .000E+00    4318.87  0.431E+00
ZONE(   5)    0.000         0.00   0.0000   .000E+00    3080.46  0.200E+00
ZONE(   6)    0.000         0.00   0.0000   .000E+00    1292.00  0.469E-02
ZONE(   7)    0.000         0.00   0.0000   .000E+00     254.87  0.952E-05

COMPONENT= OP-XYLENE

        FREUNDLICH K (um/g)*(L/um)**1/n :       895.00
        FREUNDLICH 1/n :                         0.2587
        INITIAL CONCENTRATION (ug/L) :           9.3000
        MOLECULAR WEIGHT :                     106.1700
        SINGLE SOLUTE TREATMENT CAPACITY
          (mg CARBON/L WATER) :                  0.1838
        DIMENSIONLESS BED LENGTH
          FOR ZONE( 2) :                       0.00548393
```

```
            C(ug/L)      Q(ug/g)    C/Co       DG          QAVE    Clo (ug/L)
ZONE(  1)     9.300     23999.72  1.0000  .274E+07    23999.72  0.255E+02
ZONE(  2)    13.302     49639.81  1.4303  .396E+07    34705.43  0.164E+02
ZONE(  3)     0.000         0.00  0.0000  .000E+00    23622.96  0.368E+01
ZONE(  4)     0.000         0.00  0.0000  .000E+00     7724.14  0.125E+01
ZONE(  5)     0.000         0.00  0.0000  .000E+00     5509.29  0.603E+00
ZONE(  6)     0.000         0.00  0.0000  .000E+00     2310.69  0.171E-01
ZONE(  7)     0.000         0.00  0.0000  .000E+00      455.82  0.473E-04

COMPONENT= ETHYL BENZENE

          FREUNDLICH K (um/g)*(L/um)**1/n :       714.40
          FREUNDLICH 1/n :                        0.2953
          INITIAL CONCENTRATION (ug/L) :          4.5000
          MOLECULAR WEIGHT :                    106.1700
          SINGLE SOLUTE TREATMENT CAPACITY
            (mg CARBON/L WATER) :                 0.1509
          DIMENSIONLESS BED LENGTH
            FOR ZONE( 3) :                    0.00616167

            C(ug/L)      Q(ug/g)    C/Co       DG          QAVE    Clo (ug/L)
ZONE(  1)     4.500      2898.63  1.0000  .683E+06     2898.63  0.102E+03
ZONE(  2)     4.693      4137.38  1.0430  .935E+06     3415.85  0.693E+02
ZONE(  3)    11.638     30052.06  2.4796  .274E+07    11921.58  0.187E+02
ZONE(  4)     0.000         0.00  0.0000  .000E+00     3898.07  0.729E+01
ZONE(  5)     0.000         0.00  0.0000  .000E+00     2780.32  0.385E+01
ZONE(  6)     0.000         0.00  0.0000  .000E+00     1166.12  0.170E+00
ZONE(  7)     0.000         0.00  0.0000  .000E+00      230.03  0.972E-03

COMPONENT= TOLUENE

          FREUNDLICH K (um/g)*(L/um)**1/n :       475.00
          FREUNDLICH 1/n :                        0.3282
          INITIAL CONCENTRATION (ug/L) :         19.3000
          MOLECULAR WEIGHT :                     92.1500
          SINGLE SOLUTE TREATMENT CAPACITY
            (mg CARBON/L WATER) :                 0.7365
          DIMENSIONLESS BED LENGTH
            FOR ZONE( 4) :                    0.03971676

            C(ug/L)      Q(ug/g)    C/Co       DG          QAVE    Clo (ug/L)
ZONE(  1)    19.300      2588.85  1.0000  .142E+06     2588.85  0.427E+03
ZONE(  2)    19.431      3430.54  1.0068  .187E+06     2940.29  0.301E+03
ZONE(  3)    21.074      9559.21  1.0845  .481E+06     5053.90  0.926E+02
ZONE(  4)    26.582     23550.82  1.2614  .939E+06    17502.77  0.396E+02
ZONE(  5)     0.000         0.00  0.0000  .000E+00    12483.96  0.223E+02
ZONE(  6)     0.000         0.00  0.0000  .000E+00     5235.99  0.134E+01
ZONE(  7)     0.000         0.00  0.0000  .000E+00     1032.88  0.129E-01

COMPONENT= TETRACHLOROETHENE
```

```
                  FREUNDLICH K (um/g)*(L/um)**1/n :         435.00
                  FREUNDLICH 1/n :                          0.3847
                  INITIAL CONCENTRATION (ug/L) :           37.6000
                  MOLECULAR WEIGHT :                      165.8300
                  SINGLE SOLUTE TREATMENT CAPACITY
                    (mg CARBON/L WATER) :                   0.9225
                  DIMENSIONLESS BED LENGTH
                    FOR ZONE( 5) :                      0.02372424

                     C(ug/L)     Q(ug/g)    C/Co        DG          QAVE   Clo (ug/L)
      ZONE(   1)      37.600     3325.51  1.0000   .938E+05      3325.51  0.116E+04
      ZONE(   2)      37.732     4171.96  1.0035   .117E+06      3678.94  0.864E+03
      ZONE(   3)      39.120     9349.41  1.0368   .253E+06      5489.69  0.316E+03
      ZONE(   4)      42.300    17429.04  1.0813   .437E+06     13525.16  0.153E+03
      ZONE(   5)      86.028    53746.99  2.0337   .662E+06     25058.53  0.938E+02
      ZONE(   6)       0.000        0.00  0.0000   .000E+00     10509.99  0.854E+01
      ZONE(   7)       0.000        0.00  0.0000   .000E+00      2073.26  0.163E+00

      COMPONENT= TRICHLOROETHENE

                  FREUNDLICH K (um/g)*(L/um)**1/n :         192.00
                  FREUNDLICH 1/n :                          0.4328
                  INITIAL CONCENTRATION (ug/L) :           47.9000
                  MOLECULAR WEIGHT :                      131.2900
                  SINGLE SOLUTE TREATMENT CAPACITY
                    (mg CARBON/L WATER) :                   2.9398
                  DIMENSIONLESS BED LENGTH
                    FOR ZONE( 6) :                      0.11452885

                     C(ug/L)     Q(ug/g)    C/Co        DG          QAVE   Clo (ug/L)
      ZONE(   1)      47.900      605.60  1.0000   .134E+05       605.60  0.645E+04
      ZONE(   2)      47.920      732.64  1.0004   .162E+05       658.64  0.494E+04
      ZONE(   3)      48.105     1421.89  1.0039   .313E+05       902.37  0.203E+04
      ZONE(   4)      48.441     2277.43  1.0070   .499E+05      1827.82  0.106E+04
      ZONE(   5)      49.742     3357.60  1.0268   .716E+05      2266.48  0.687E+03
      ZONE(   6)      77.244    19649.73  1.5529   .270E+06     12358.89  0.817E+02
      ZONE(   7)       0.000        0.00  0.0000   .000E+00      2437.98  0.241E+01

      COMPONENT= CIS-DICHLOROETHENE

                  FREUNDLICH K (um/g)*(L/um)**1/n :          46.90
                  FREUNDLICH 1/n :                          0.5562
                  INITIAL CONCENTRATION (ug/L) :           70.9000
                  MOLECULAR WEIGHT :                       96.9300
                  SINGLE SOLUTE TREATMENT CAPACITY
                    (mg CARBON/L WATER) :                  18.5590
                  DIMENSIONLESS BED LENGTH
                    FOR ZONE( 7) :                      0.80273451

                     C(ug/L)     Q(ug/g)    C/Co        DG          QAVE   Clo (ug/L)
      ZONE(   1)      70.900      107.47  1.0000   .161E+04       107.47  0.397E+05
      ZONE(   2)      70.902      122.53  1.0000   .183E+04       113.76  0.323E+05
      ZONE(   3)      70.922      194.39  1.0003   .291E+04       139.51  0.161E+05
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ZONE(  4)    70.951       268.11  1.0004    .401E+04      226.06  0.977E+04
ZONE(  5)    71.049       349.88  1.0014    .522E+04      261.56  0.695E+04
ZONE(  6)    71.862       831.43  1.0114    .123E+05      592.42  0.133E+04
ZONE(  7)    85.589      4242.03  1.1910    .526E+05     3522.09  0.856E+02
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